Investigation of a Reproducible Boiling Phenomenon with Relevance to Volcanic Lightning

Thesis

Investigation of a reproducible boiling phenomenon with relevance to volcanic lightning.

A thesis presented for the degree of

DOCTOR OF PHILOSOPHY

of the

OPEN UNIVERSITY

in the

FACULTY OF SCIENCE

by

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October 1978.

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Abstract.

Evidence for the existance of volcanic lightning is produced from a literature survey and the charge sources which have been suggested are listed and those, of the 18th and 19th centuries, which involved boiling water are reviewed in detail. Studies of saline contact charging, undertaken by Blanchard et al, when Surtsey emerged in 1963 are reviewed and lead to the continuation, in this investigation, of the Leidenfrost form of boiling and the discovery of an associated charging process. This discovery resolves a two centuries long dispute as to whether the Leidenfrost phenomenon of boiling produces charge as well as showing its important relevance to volcanic lightning where solution contact charging is in evidence.

The mechanisms by which charged particles are emitted and formed into hollow solute spheres have been investigated and their charge and size distributions determined. Their structure has been compared with the structure of particles produced by flash boiling and spraying of saline solution. The energy conversion involved in the particle emission mechanism has also been studied.

Charging mechanisms and some charging processes have been reviewed and by comparing results from other investigations speculations as to which mechanisms produce charge in the Leidenfrost process have been attempted. The comparison of results leads to the suggestion that Blanchard's observations are more likely to be Leidenfrost boiling than, as he assumed, flash boiling. The high average charge per particle of 10^{-14}C on particles from Leidenfrost boiling indicate that the number density is smaller, by a factor of 10^{4}, than that previously suggested to produce the fields measured in volcanic clouds.

Exploratory experiments have established that in addition to saline solution other aqueous solutions will also produce charge.

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Introduction.

'Great Surtur with his flaming sword,
Southward at Muspel's gate kept ward.
And flashes of celestial flame
Life giving from the fire world came.' Valhalla, J.G. Jones.

Few things could be more awe inspiring than a volcano, with its attendant lightning, emerging from the ocean depths. Lightning, which in common with many people I view with both fear and fascination, offers an opportunity to study electricity and natural phenomena. In reading F.W. Lane's book, 'The Elements Rage - the extremes of natural violence' I learned of another, and seemingly new or neglected, manifestation of it which occurs above erupting volcanoes. The outcome of exchanging a few letters was a new interest in volcanic electricity and in particular one possible source in the contact of sea water or other aqueous solutions with heated surfaces.

The old Norse creation story tells of a world of ice fed from a spring. This ice world was separated from a world of fire by a chasm illuminated by flashes as sparks fell from the sword of the giant Surtur on to the ice in the abyss. It seemed appropriate that the volcano which launched the first investigations of saline contact charging should be named Surtsey. It was my reading of the activities of Surtsey and of these early investigations which started my interest.

Of course Surtsey was not the first island of its kind. The Liber Miraculorum of Herbert of Clairvaux (1178) mentions volcanic islands bursting from the depths of the sea, and even earlier the terrified sailor monks in St. Brendan's oxhide boat sailed by such an island off Iceland trying to comfort themselves with the dictate, "Soldiers of Christ, be strong in faith unfeigned and in the armour of the Spirit, for we are now on the confines of hell." It must have worked since the story has been preserved!

The existance of volcanic lightning poses many questions: Is it a rare phenomenon ? What charge sources have been proposed to account for it ? What investigations have been made of the part played by water in electrical charge production ? Have the phenomena of charge production from boiling, with hints of the existance of some particle, been fully

investigated ? These questions and others arising from them provided and maintained my interest to pursue the aims (set out in the following flow chart and introductory summary) which culminated in this thesis.

Summary of aims.

(Chapter 1) (Pages 10- 20

Since volcanic lightning has been the underlying motivation for this work, it is important to establish the evidence for its existance. The aim of the first chapter is to do this by descriptions from historical sources, and from more recent eye witness accounts, sometimes with the additional advantage of photography. Unfortunately what is perhaps the most famous volcanic lightning photograph, that over Surtsey by Jonasson, is now thought to show in part an atmospheric thunderstorm in the immediate vicinity of the volcano.(1) There are however at least two excellent photographs, one of Vesuvius(1944)(Page 13 (Photograph 1 chapter 1) and one of Cerro Negro(1972) (Photograph 2 (Page 16 chapter1). At the present time no provision is made on report forms to Volcanological Societies(2) to record observations of lightning, so there is no way to compare the number of eruptions to the count of lightning observations, and thereby give an accurate statement on the frequency of lightning occurrence.

(Chapter 2) (Pages 21-37

Several possible sources of charge have been suggested for volcanic lightning and these are all described in the opening section of chapter 2. They are not subjected to any comment; (Pages 21-24 the aim simply being to bring them together into one place. The author's introduction to charging associated with boiling saline solution is followed by details of how water can reach a volcano since an investigation of aqueous solution charging is only a plausible undertaking if this occurs. Published material on investigative work of the late eighteenth to late nineteenth centuries on

electricity from various forms of boiling is brought together, possibly for the first time, in the final sections of this chapter. (Page 26-32 (Chapter 3) (Pages 38-45

Surtsey emerged from the sea on November 14th 1963 and field work was carried out to measure electrical fields in steam. One member of the expedition to Surtsey was D.C. Blanchard who, in a letter to Nature, later explained a saline solution charging process. Several publications by Blanchard and others followed this first letter and references were made to the earlier paper by Woodcock and Spencer relating to the production of salt (Page 38 particles when sea water contacts molten lava. In the third chapter all papers on saline solution charging are reviewed and their results summarised and appraised. The discovery (Page 39-44 of the charging phenomenon which exists when drops exhibit Leidenfrost's form of boiling had its origin in the author's planned continuation of the work of Blanchard and his co-workers.

(Chapter 4) (Pages 46-66

J.G. Leidenfrost published details of the boiling phenomenon which now bears his name; in 1756. The phenomenon appears to have been little studied (except for demonstrations of it by Tyndall (1870), and some work to explain drop appearances, by (Page 49 Garnett in 1879) until some investigations were made from an engineering standpoint in America during the 1960s. (Page 50 A review of this material leads to the author's investigation of the Leidenfrost phenomenon made in order to try and understand the charging phenomenon found to be associated with it. Photography aided the qualitative descriptions of drop behaviour and the particle emission mechanism. (Page 57

(Chapter 5) (Pages 67-80

Evaporation times were measured for drops of different volumes and empirical relations obtained relating drop volume to time and evaporation rate. The thickness of the supporting vapour layer (Page 70 was determined and the pressure in the layer calculated. An attempt was made to relate evaporation rate to the flow of vapour (Page 74 from the layer on the basis of treating the gap between the drop and the heated surface as an annular orifice.

(Chapter 6) (Pages 81-114

The particles proposed by Woodcock and Spencer as raindrop nuclei were not described as to their formation or structure and this anomaly was not corrected by Blanchard or others. One of my major aims is to describe the structure of salt particles also how they were emitted from a Leidenfrost drop and how they are formed from solution. The number of particle emission bursts, and the number of particles emitted, were counted. The size (Page 92 distribution of particles was obtained by optical microscopy and the use of dark field photography. The structure of particles (Page 98 was compared to that of particles obtained by flash boiling (the form of boiling taken by solution in the work of Woodcock and Spencer) and particles from an aerosol spray. (Page 101

I made subsidiary experiments on the little understood or studied phenomenon of crystalline decrepitation. (Page 87

Empirical equations relating time of first particle emission to drop volume and solution concentration were obtained from volumes of 3.5% Na Cl $_{(aq)}$ solution drops. (Page 90

(Chapter 7) (Pages 115- 126

Chapter 7 contains details of the electrical activity associated with drops and particles. That solution drops exhibiting the Leidenfrost phenomenon generated electricity was the subject of conjecture , with affirmation alternating with denial,

for nearly two centuries. The dispute has been resolved by this investigation. In 1870 Tyndall had demonstrated that the vapour layer was an insulator. An exploratory chart record of the resistance properties of the layer was made as part of the present investigation. The fact that each particle emission is (Page 116 accompanied by a pulse of electricity had already been exploited to count the number of particle emissions before obtaining records of the pulses themselves for study with regard to charge magnitude and duration. Knowledge of the amount of charge accompanying a particle emission, and the number of particles emitted, made it possible to estimate the average charge carried by an individual (Page 118 particle.

The charge distribution was obtained from negatives of tracks of particles falling through an electric field under gravity in stroboscopic light using a dark field ultramicroscope. The (Page 121 effect on charge of the kind of material forming the heated surface was considered in preparation for speculation on the charging process which may be operating.

(Chapter 8) (Pages 127-132

The investigation, arising as it did from saline contact charging, was confined to $Na\ Cl_{(aq)}$. Although it seemed likely that the majority of volcanoes might be considered to involve saline solution only, several other, possibly non-saline, water sources had been suggested since not all volcanoes are situated on the sea shore, nor are they islands emerging from the ocean floor. In order to determine if the charging phenomenon involving Leidenfrost drops of salt water also occurred with other aqueous solutions and so make other water sources relevant to any future investigations, a series of exploratory experiments were made using other solutions. The aim of chapter 7 may be summarised as seeking to answer three questions (i) Do aqueous solutions other than $Na\ Cl_{(aq)}$ produce

electricity ? (ii) If so do they produce charge from Leidenfrost drops and the Blanchard effect ? (iii) Does the flash boiling of aqueous solutions produce charge ?

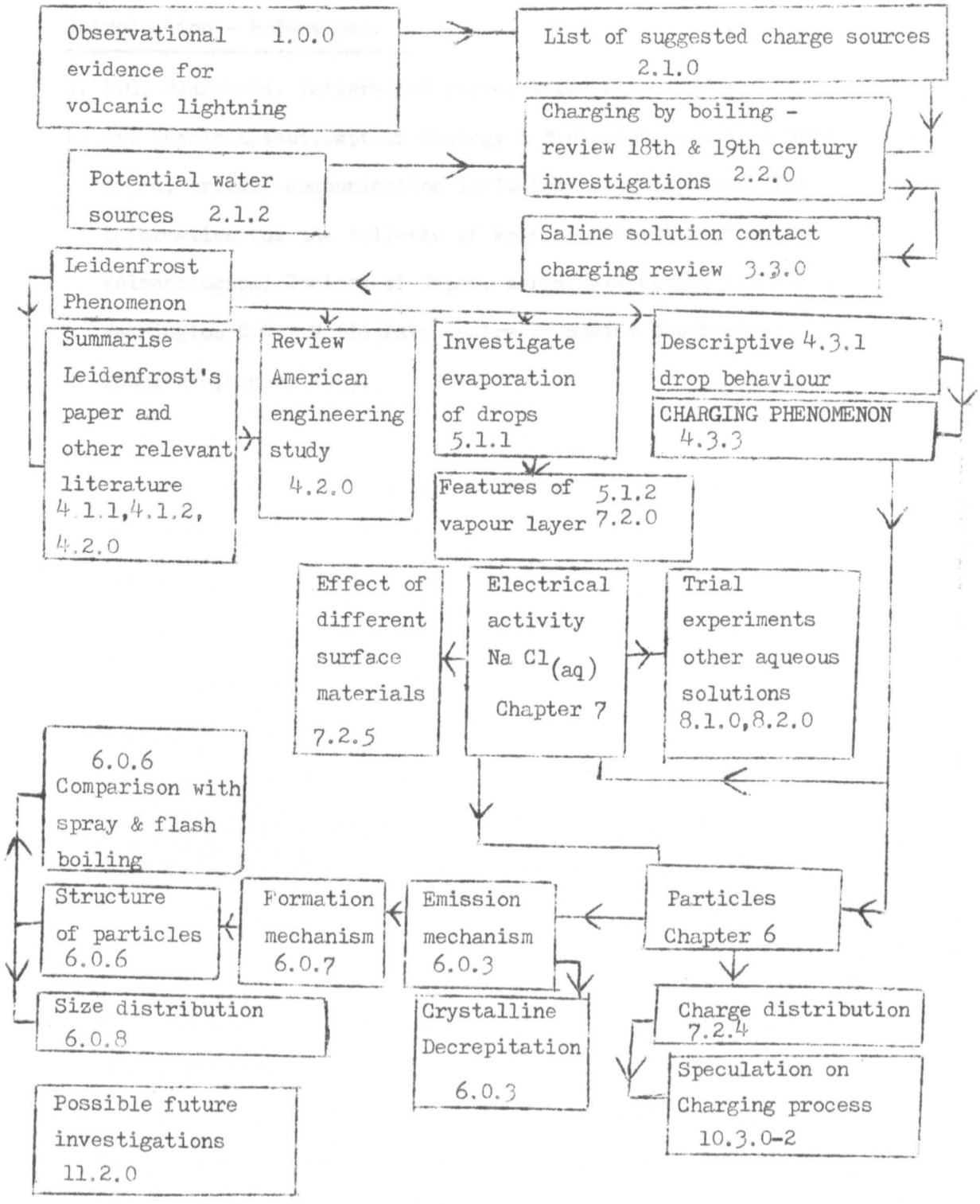
(Chapter 9) (Pages 133-159

The results of the investigation led to speculation on the source of electrical charge, and to help with this an outline review of present knowledge of charging processes is presented in the ninth chapter. The word processes is used in preference to mechanisms. Mechanism implies an explanation, in terms of basic physics, of the origin of charge. Process focusses on a particular phenomenon in which there is production of charge but without being able to go so far as to isolate the physical mechanism and at the present time seems the wiser choice of term. Processes may, for the most part, be placed into sets each set having the charateristic property of a particular hypothetical charging mechanism as the source of charge produced in each process in the set.

(Chapter 10) (Pages 160-174

Chapter 10 covers speculation on which charging mechanism or mechanisms may be operating in the Leidenfrost charging process. Processes are classified according to the charge per particle, and the charge/mass ratio of particles in an attempt to say which (Pages mechanisms might be operating. The energy per particle emission is considered.

(Chap.11) Results from Leidenfrost particle investigations are (Pages 175-178 compared with the earlier results from saline charging made by Blanchard et al and the suggestion made that the boiling phenomenon observed by Blanchard may be producing charged particles by the Leidenfrost phenomenon and not, as Blanchard assumed, by flash boiling of solution. (Page 176



The components of an investigation of a reproducible boiling phenomenon with relevance to volcanic lightning.

Introduction - References.

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1.0.0 Evidence for the existance of volcanic lightning and its relevance to an investigation of a reproducible boiling phenomenon.

1.0.0 Introduction.

This thesis presents the results of an investigation of a boiling phenomenon and the discovery of an associated charging process but no part of it directly investigates lightning so why then does the title include volcanic lightning ?

The investigation evolved from work carried out, about a decade ago, into saline solution contact charging in the laboratory follow up to field work on the lightning observed above the volcano Surtsey. Material obtained from this recent investigation has been compared to the earlier Surtsey results thereby bringing it back to its origin in volcanic lightning.

Also, bearing in mind the controversy surrounding the existance, or otherwise, of ball lightning and the somewhat embryonic status of the study of volcanic lightning I feel that it is necessary to collect together in one place both observational and investigative evidence to establish the validity of the latter. Should volcanic lightning exist then the laboratory demonstrations are of relevance to a spectacular natural phenomenon. It was on the acceptance of the existance of volcanic lightning that twentieth century investigations of charging from boiling solutions arose. Had this not been the case it seems likely that these charging phenomena would have remained little studied save in the 'steam electricity' investigations of earlier times. But evenso they too accepted its existance (see chapter 2) and pondered on boiling phenomena as contributory charge sources.

Volcanic lightning and a reproducible boiling phenomenon are, in this thesis, relevant to each other for the reasons stated, hence the title, and the subject matter of this first chapter. Information relating to volcanic lightning will appear again in chapter 11 where the relevance of this investigation is considered in a quantitative manner.

1.1.0 Volcanic Lightning - Earliest Historical Accounts ?

'There were thunders and lightnings and a thick cloud upon the mountain.' Exodus ch 19 v 16

In 1965 core samples obtained in the vicinity of Santorin[1] gave rise to investigations and speculation linking an explosive volcanic eruption with the sudden ending of Minoan Crete, Legendary Atlantis [2] and the Hebrew exodus. [3,4]

J.V. Luce [5] brought in references from Classical writers including, from Hesiod's Theogany (c 735 B.C.), "The heat of thunder and lightning and of fire from such a monster, the heat of the fiery storm winds and flaming thunderbolt. And the whole earth and sea boiled." From Pindar's Paean (c 460 B.C.), "The heavy sounding war between Zeus and Poseidon. Once with thunderbolt and trident -----." Luce interprets these to refer to the violent electrical activity during the eruption of Thera which carbon dating indicated to have occurred in 1470 B.C.,thereby perhaps making this the earliest reference to volcanic lightning.

Blanchard [6] is of the opinion that Lucretius [7] refers to volcanic lightning, "The fire of Etna to overflow, the heaven to be in flames: for that too is seen and the heavenly quarters are on fire."

1.1.1 Some lightning and other electrical observations during eruptions.

Volcanic lightning is not uncommon, but unfortunately references to it are scattered and the aim of this section is to bring together some of the descriptions with the objectives of proving its existance, indicating its appearance and the existing conditions at the time of the observations.

Vesuvius

At about one o' clock in the afternoon of August 24th 79 A.D., Pliny the Younger describes an eruption in which, "Most intense darkness was rendered more appalling by the fitful gleam of torches at intervals obscured by the transient blaze of lightning." (8)

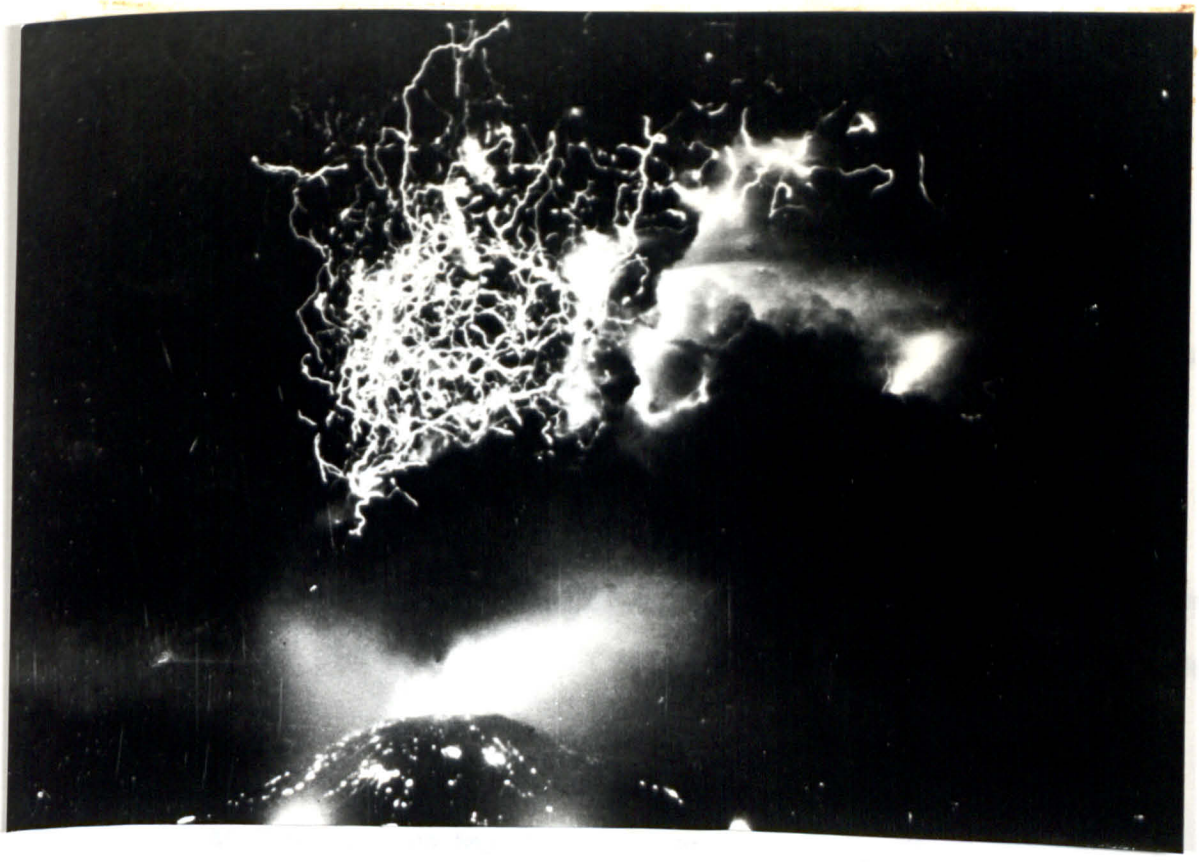
The eruption of 1707 produced lightning from the mouth of the crater described as resembling that seen in tempests but assuming a, "more twisted and serpentine form." (9)

An eruption in 1872 saw the first attempt to investigate charges in clouds from a volcano.(10) Palmieri found that steam clouds carried positive charge and ash clouds a negative charge and mixed clouds charges of both polarities.

A new, possibly electrical, phenomenon appeared in the activities which started on April 7th 1906. Named the flashing arc and described as a yellowish 'ionised' light flashing, "at lightning speed from the crater at the height of the eruption", along with "St. Elmo's fire and other forms of lightning".(11)

One description of 'The Pine', the Italians' name for the mushroom shaped cloud above Vesuvius mentions, "In the column, but more frequently in the cloud above it, flashes of forked lightning are seen every moment in all directions and are accompanied by thunder." (12)

In March 1944 the latest eruption of Vesuvius occurred when Photograph 1 (next page) was obtained. Wing Commander Shore (13) who flew through the 20,000 ft high cloud on March 27th stated that lightning forked at a height of 8,000 ft.



Photograph 1 Lightning above Vesuvius in eruption March 1944

Official U.S. Air Force Photograph.

At the bottom of the picture molten lava may be seen on the sides of the ash cone. Above the cone the glow from the crater is seen on the underside of the ejectamenta cloud. The time exposure shows lightning of the, "twisted and serpentine form", in the cloud above the volcano.

Krakatoa

Captain Woolridge of the "Sir Robert Sale" described the cloud at 4 a.m. on August 26th 1883 as having, "The appearance of an enormous pine tree the stem and branches formed with violent lightning" and also, "An immense wall with bursts of forked lightning at times like large serpents rushing through the air". A ship lying 45 miles off was struck by lightning five times on the mainmast conductor.(14)

The Royal Society expedition reported, "A terrible storm of a strictly local character, which raged during the whole time of the eruption. The electrical disturbances, resulting in vivid lightning, fireballs, corposants" (Corona glows - St.Elmo's Fire):(15)

Other Instances.

That volcanic lightning may be as fatal as that of a thunderstorm was shown when Katlagia, in Iceland, erupted in 1755. "Zig zag lightning from the steam cloud killed eleven horses and two men and pierced cylindrical holes in some rocks in the way of the group." (16,27)

At 7.50 a.m. on May 8th 1902 the side of Mt. Pelee volcano opened and a horizontal black cloud emitting noises like gunfire from continuous lightning reached the town of St. Pierre, five miles away, within seconds and 30,000 people perished. (17)

The lightning produced in the clouds over Paricutin, the volcano which came up through a Mexican cornfield, was observed to occur at intervals of one to five minutes. The flashing arc first recorded at Vesuvius in 1906 was also observed.(18)

On June 13th 1811 Captain Tillard witnessed a column of smoke rising from the sea N.W. of San Miguel.(19) Flashes of lightning from this cloud were followed by thunder which was compared to continual firing of guns and muskets. By July an island had emerged from the sea to a height of 300 feet and a circumference of 1 mile but a large crack through the island allowed access for the sea, "from which water in a high state of ebullition was continually and rapidly flowing."

The charge distribution in the cloud above Volcano Azuma was determined in August 1950 by a Japanese expedition. The charge was found to be positive, which induced a weak negative charge around the outside of the cylindrical cloud.(20)

Cerro Negro in Nicaragua was in violent eruption in 1971 and electrical phenomena was recorded, "inside the cloud, between the cloud and the crater or main cone." Penalba obtained the excellent time exposure photograph Photograph 2.(21)

Of major importance to this investigation was the emergence of the island volcano Surtsey at 6.30 a.m. on the morning of November 14th 1963. Vivid lightning was observed and an American expedition studied the situation and measured charge in the clouds associated with the volcano.(22,23)

Helgafjell erupting at Heimey in the Vestmann Islands in 1973 is the latest to be observed from the point of view of obtaining charge measurements and lightning photographs.(24,25,26,27)

1.1.2 'Volcanic Electricity in Connection with Eruptions in Iceland'.

One of the most comprehensive descriptions of the electrical activities and conditions prevailing at the time of eruptions of volcanoes of various types is to be found in a paper by Thorarinsson,(28) Many observations given by Thorarinsson have an important bearing on this investigation. A brief summary of the paper follows.

Following the field work at Surtsey Thorarinsson searched Icelandic literature relating to eruptions and brought together all references to electrical activity.

The 1625 eruption of Katla from beneath 500m of glacial ice produced much corona described as enveloping people and cattle, "in one continuous fire or blaze." On, "Hats and garments there was seen so much glowing fire as if we were enveloped with flame or glowing coals. Yet it was not the colour as of our natural fire, but rather had the appearance of the shimmer on newly caught fish or that which some call corpse light or carrion flame. Said fire or flame swept or flew

Photograph 2. Lightning above Cerro Negro, Nicaragua.

Ing. Penalba. Courtesy of Smithsonian Institute for Short Lived Phenomena. The molten lava may be seen showing against the dark material of the cone. Lightning is obvious and of particular interest must be the horizontal discharge with many side branches. The cloud is lit up both by lightning and the reflected glow of lava streams in the left of the picture. Star trails may be seen in the upper left of the photograph.

along the ground as well as through the air, so that all seemed aflame at the moment when it appeared."

Descriptions of St. Elmo's fire or corona with its cold fire appears in many accounts and was witnessed streaming like flames from weathercocks on farms and iron poles on churches, "without the poles being warmed".

The frequency of occurrence of lightning and thunder was noted in several instances and includes details of Thorarinsson's own experience on Hekla.

The summary of the paper makes it clear that electrical phenomena at Surtsey do not seem to differ from those seen at the subglacial volcanoes Katla and Grimvötn, and the chemical composition of the magma is the same. It is further noted that the occurrence of lightning is of greater frequency where water is present, that is in a phreatic eruption, as against one, such as Hekla, in which tephra production is very high. Thorarinsson states that this difference, "is particularly striking as regards the violent initial phase when tephra uprush is at its maximum." The lava of Hekla being very acid he postulated that this may play some part in the lower frequency of occurrence of electrical activity but then calls to mind contrary evidence in the lightning observed at Komagatake (Japan) in 1929 where lava was also very acid. (Lightning has also been witnessed in the clouds from Anak Krakatoa which has a very acid lava.[29]

The paper concludes that it is of interest to note that both in the case of the acid and basic eruption electrical phenomena are noticed at a great distance from the volcanoes.

The 1973 eruption at Heimey, of a fissure volcano, had at one stage a lava flow rate, at one place, of 100 m^3 s^{-1} into the sea (Moore [27]) which produced turbulent clouds carrying positive charge. A positive potential gradient was produced, in one instance 7 x 10^3 V m^{-1}. Lightning was reported throughout the sea water lava contact period and

Moore and his co-workers recorded eight instances in which positive charge was lowered to earth. A magnificent intracloud discharge accompanied by thunder was observed but the investigators had just taken down their apparatus and no record either of the potential gradient or by means of a photograph was obtained!

1.2.0 Concluding comments.

Lightning associated with volcanic eruptions is clearly not a rare phenomenon. Some efforts have been made to record it on photographs and measurements of potential gradients and some prevailing conditions are known. Blanchard [30] reported that on approaching Surtsey 'an eerie silence prevailed ----- then every so often a sudden sharp crack like a rifle shot'. On approaching nearer it was found that the sound was thunder associated with individual flashes of lightning from steam clouds. Moore et al [27] took particular note of the lightning at Heimey and reported that the potential gradient reversals of volcanic lightning are opposite to those of atmospheric thunderstorms i.e.a vertical column of positive charge is neutralised by an upward moving discharge without stepped leaders -"Producing thunder the sound of which was anomolous in that it was a short sharp crack similar to the sound produced by a single spark from a large van de Graaff generator". In thunderstorms the discharge is usually downwards first by a stepped leader and then a return stroke.

They felt that although they had extended the earlier Surtsey work several important questions remain unanswered viz. "What is the polarity of the initiating streamer? Is there a leader return stroke sequence? (I asked Moore if a Boys camera could be used to resolve the question of discharge structure. In the case of Heimey this apparently would have been impossible due to snow and falling tephra and also possibly the infrequency of the lightning but may have worked at a more recent eruption -Augustine Island Alaska (1976) but unfortunately no expedition went there.) Having established evidence for the existance of volcanic lightning consideration may now be given to ideas proposed as sources of charge.

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2.0.0 Charge sources - First considerations.

2.1.0 Suggested charging sources.

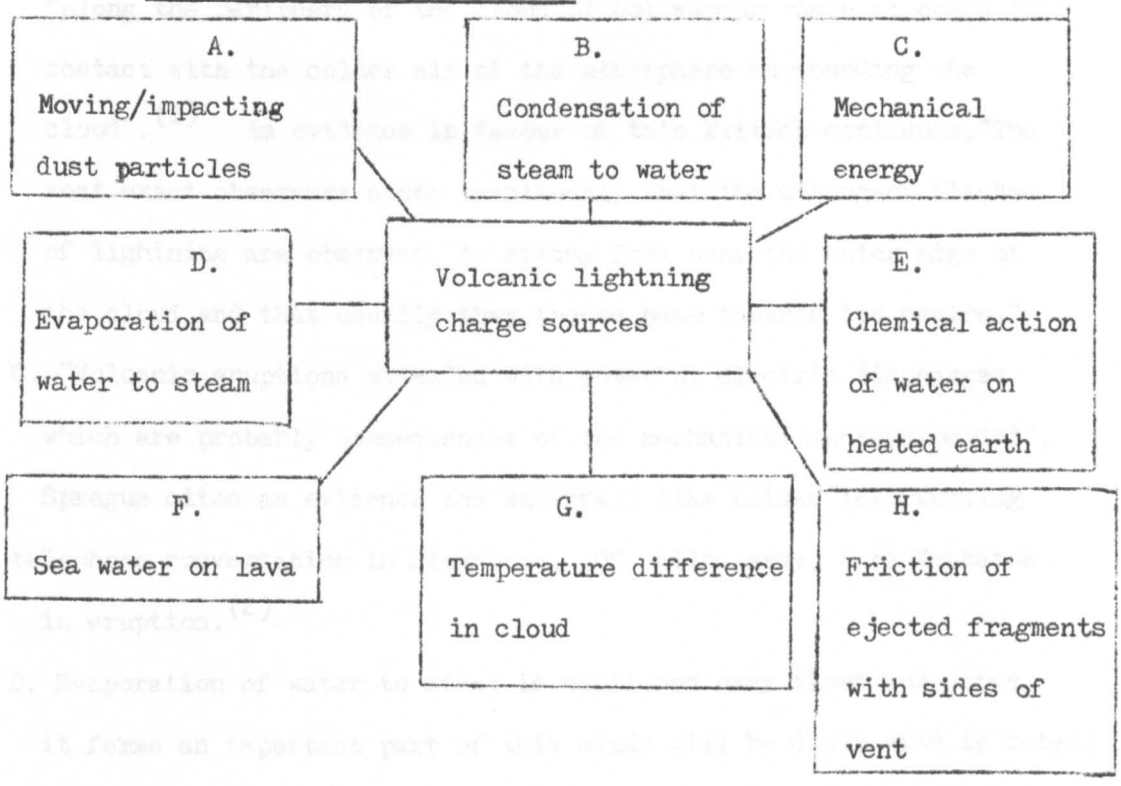


Chart 1

The chart shows suggested sources of electricity in volcanic clouds. There is an unfortunate tendency in some early accounts to attach a charging mechanism or process almost as an afterthought and because of this it is difficult to give much credence in some instances. By way of reference each of the above is listed, below, with its source.

It is not claimed that this is an exhaustive search of literature the main idea of this section being to convey some of the range of suggested charge sources put forward by observers of volcanic lightning.

A. Moving or impact of dust particles is suggested in several early accounts but more recently in the eruption of Paricutin and Cerro Negro (1971) (see refs. 18 & 21 chapter 1).

B. Condensation of steam to water is referred to as being without doubt, "along the periphery of the cloud of hot vapour where it comes into contact with the colder air of the atmosphere surrounding the cloud".(1) As evidence in favour of this Wittich continues,"The most exact observers state unanimously that the strongest flashes of lightning are observed to spring from near the outer edge of the cloud and that usually they thence pass towards its centre."

C. "Volcanic eruptions attended with powerful electric discharges which are probably consequences of the mechanical energyexpended". Sprague cites as evidence the waterfall like noises interrupting telephone conversation in Singapore, 500 miles away, from Krakatoa in eruption.(2)

D. Evaporation of water to steam is mentioned many times and since it forms an important part of this study will be dealt with in detail later in this chapter.

E.Chemical action of water on heated earth is mentioned in conjunction with mechanical energy (see ref. 2). No explanation is given as to what the chemical action might be.

F.Sea water acting on lava was demonstrated to produce charge, by Blanchard, and will be dealt with later (Chapter 3).

G.The report on Cerro Negro cites the temperature difference inside the cloud, without explanation, along with dust impact as a charge source (see ref 21 chapter 1)

H."The friction between the ascending column of vapour, the ejected fragments and the sides of the vent gives rise to the generation of electricity and the wonderful displays of lightning so common during volcanic outbursts". This is how the Geologist Lyell explained the phenomenon.(3)

2.1.1 Comments on charging sources - leading to this investigation.

Repeats of the experiments of P.E. Shaw on triboelectrification led me to believe that dust impacts caused the lightning seen above erupting volcanoes.[4,5,6,7] However a footnote in Lane (see ref 11 chap.1), in which C.B. Moore had stated that observations at Surtsey showed that electricity was not generated in the clouds above the volcano and that the material from the crater was already charged led to my interest being redirected. An exchange of letters with Moore, in which he suggested that I read of the laboratory work carried out by Blanchard led to an ongoing exchange of letters with Blanchard. Study and continuation of Blanchard's work launched this investigation.

This is not to suggest that the other sources of charge shown in chart 1 are less worthy of consideration but interest directed the course of the investigation into, as it turned out , a relatively unexplored field. Starting in the first instance to investigate electrification due to saline water contact with heated surfaces the investigation rapidly focussed on to one aspect in particular, and from the results gained opened out again to be applied to charging from boiling solutions.

Consideration will now be given to earlier work on electricity produced during evaporation, not only to take account of results but also to put this investigation into its historical context and collect together the published investigations of the 18th and 19th centuries.

First it must be established that volcanoes do produce component materials to make solution contact charging a plausible charge source for volcanic clouds.

2.1.2 Evidence of component materials from or in proximity to volcanoes.

Various water sources are available to produce steam. The ancient legend which says that water sucked down in the whirlpool Charybdis appears as steam from Etna[8] was referred to by Lucretius[9]. Fouqué calculated that Etna erupted 2.1 x 10^6 m^3 of water in 100 days.[10] Holmes[11] (1965) states that steam is the most common volcanic gas estimated to be 60% to 90% of ejected material. More recently Francis (1976)[12] and Krafft (1976)[13] have stated that volcanic steam is 90 to 95% water and 5 to 10% Carbon dioxide, Hydrogen sulphide, Boric acid, methane, hydrogen, and trace elements. Thermal springs in the vicinity of volcanoes have been found to contain silica, calcium, magnesium, strontium, potassium, lithium, chlorine, fluorine, bromine, iodine, boron, carbonates and ammonium sulphate. Escaping steam ranges in temperature from 100°C to 1,200°C.

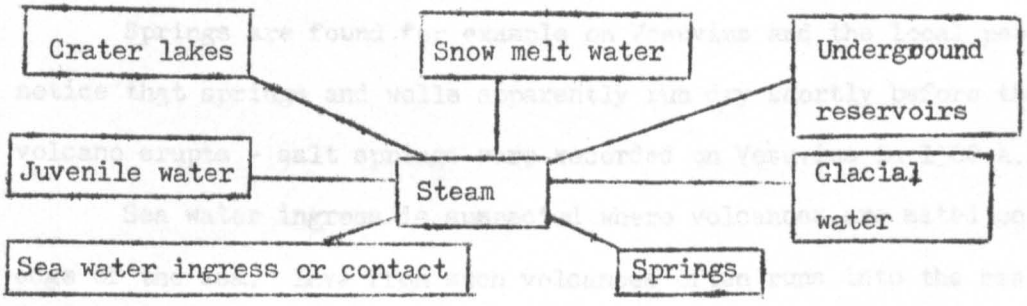


Chart 2.

Crater lakes are not pure water but aqueous solutions with a wide range of concentrations. By way of example Kawah Idjen (Java, Indonesia) is estimated to hold 36 million tons of H_2SO_4 and H Cl plus 1 million tons of potassium and 300,000 tons of alum and 200,000 tons of aluminium in its crater lake (see Krafft[13]). Krafft et al also state that crater lake Assal is supersaturated with Na Cl and gypsum, and that the crater lake of Vulcano is grey with white bubbles. Volcano Keli Mutu (Krafft pp 68-69) has three explosion craters each with a lake from accumulated rain and spring

water, one is clear water, another holds sulphurous emerald green water and the third is dark red due to iron salts. Oldoinyo Lengai in Africa pours out washing soda, sodium carbonate.

Snow melt water originates where volcanoes project above the snow line and may be the reason for underground reservoirs of water found in some Andean volcanoes. Humboldt [14] first described these latter and suspected that they may be upset by earthquakes during volcanic activity when the water is then released.

Glacial water is produced from subglacial eruptions and is common in Icelandic eruptions as discussed in chapter 1.

Juvenile water exists in the foundation rocks beneath a volcano and is released from the magma chamber walls during melting of the rock. Strictly speaking juvenile water should be most expected from arc type volcanoes produced where one tectonic plate is sliding beneath another. It is estimated (Krafft et al) that 1 km^3 of granite when melted will release 7×10^9 m^3 of steam.

Springs are found for example on Vesuvius and the local people notice that springs and wells apparently run dry shortly before the volcano erupts - salt springs were recorded on Vesuvius in 1500 A.D.

Sea water ingress is suspected where volcanoes are sited on the edge of the sea. Lava from such volcanoes often runs into the sea and in considerable quantities. Vesuvius in 1794 released 13 million cubic feet of lava into the sea which pushed back the shore line by 380 feet with a width of 1204 feet (see chap. 1 ref 12). Surtsey poured 180,000 tons hr^{-1} into the sea and the fissure volcano on Heimey produced 2.5×10^8 m^3 of volcanic material, 90% of which was in the form of basalt flows - between January and March 1973 - which increased the land area by 2.5×10^6 m^2 from an average sea depth of 90 m (Krafft et al). As mentioned in chapter 1 volcanic islands emerge from the sea bed and some excellent photographs of lava in contact with sea water exist. [15,16,17,18]

2.2.0 Electricity during evaporation.

Towards the end of the eighteenth century the evolution of electricity during the evaporation of liquids was demonstrated. Apart from a brief intensive investigation in the mid-nineteenth century the subject received little attention until the mid-twentieth century as a result of work on field measurements obtained at Surtsey. The present investigation is of course an aspect of the subject. A summary of the results of eleven people who examined the apparent production of electricity during evaporation, up to the end of the nineteenth century, now follows.

2.2.1 Lavoisier, Laplace and Volta 1782 (19,20)

Following a series of experiments in which dilute acids were poured on to materials such as iron filings and chalk with the consequent evolution of gas and the production of negative electric sparks attempts were next made with combustion experiments. Small dishes were filled with burning charcoal and connected to an electrometer which registered that negative electricity was present.

Volta, who was in Paris when L aplace and Lavoisier were carrying out these investigations, set up three iron furnaces and threw water on to them. He found that both polarities of electricity were produced. Subsequently he stated that negative electricity was produced by the evaporation of water.

(It is of interest to note that in one of Lichtenberg's letters[21] he mentions that Volta, who was staying with him in Göttingen, attempted to demonstrate the production of electricity from evaporating water. Nothing happened and Volta was reduced to cursing in various languages. "With no improvement", remarks Lichtenberg laconically.)

2.2.2 Horace Benedict de Saussure 1786 (19, 20)

The published investigations of Volta inspired de Saussure to study electricity from evaporation. His first experiment involved throwing red hot iron into an insulated coffee pot containing water. The results thus obtained were the opposite of those obtained by Volta so de Saussure re-arranged his apparatus to allow water to be evaporated, by boiling, from an insulated dish. The electricity produced was usually negative though variation of polarity did occur.

Water was thrown into a heated dish at diminishing temperatures. An iron 'grenade' was heated to white heat and water thrown inside (de Saussure recorded that a flame came from inside the grenade). A sheet of linen six feet square was wetted, insulated with silk cords, and hung before a fire to induce rapid evaporation. A large iron plate was placed on the ground and heated so that a great quantity of steam came off.

H.B. de Saussure's observations may be summarised:-

i Evaporation of water without ebullition does not produce electricity.

ii Water remaining stationary in a very hot dish (The Leidenfrost phenomenon) does not produce electricity.

iii Water which wets a warm surface and evaporates quietly does not produce electricity.

iv The greatest quantity of electricity is produced when the evaporating water is making the loudest noise.

v The electrical polarity for water evaporating from a heated iron or copper dish is positive. It is negative from a silver or porcelain dish (His results show that in the case of iron the polarity was sometimes different for no obvious reason.)

vi His experiments to obtain electricity from combustion failed to produce any results i.e. electricity.

(Tables of de Saussure's results may be found in Brewster [20] which are taken, in translation, from de Saussure's 'Voyage dans Les Alpes'.)

The investigations of de Saussure brought the interest to a close for half a century until a workman received a shock and drew sparks from the exhausting steam of Cramlington Colliery engine at Newcastle on Tyne in 1840.

2.2.3 W.G. Armstrong 1840 (22)

Armstrong launched the nineteenth century phase of the study of what came to be called, 'steam electricity' when he investigated the electricity from locomotive boilers.

In an attempt to determine the source of charge and relate it to the quantity of steam he made an apparatus of brass steam cocks fitted into glass tubes. It was found that sparks up to 4" long were produced as steam issued from a locomotive boiler. In the dark, corona was observed around the brass steam fittings of the locomotive. It was found that it was possible to draw small sparks from a rod held into the steam cloud collecting in the roof of the engine shed and Armstrong tried to observe if any precipitation occurred comparable to that of an atmospheric thunderstorm. He noticed that some precipitation was taking place while the rod remained insulated but when the damp affected the insulation the precipitation stopped.

He was convinced that the electricity was not produced by the expansion of steam. Probes proved that electrification did not occur inside the boiler. Only when steam issued from the jet in the apparatus was electricity produced. Armstrong was mystified by the fact that the steam was positive but the negative polarity could not be located anywhere in the apparatus.

His results led to his invention of the Armstrong Hydroelectric Generator.

2.2.4 H.L. Pattinson 1840 (23)

Pattinson investigated the electricity produced by steam exhausting from locomotive boilers, "immediately coming into the station with passengers", or lifted on to blocks of dry wood.

He made the following observations :-

i Length of spark is proportional to steam pressure (4" sparks at 52 lbs in^2, barely perceptible at 5 lbs in^2.)

ii The atmosphere in the engine shed became charged positive.

iii In a repeat of Volta's experiment a hot cinder placed on the cap of a gold leaf electrometer and water dropped on to it to produce negative electricity. This was repeated on a larger scale with an iron pan of hot cinders and water.

iv A conclusion was drawn that electrification took place at the instant of **vaporisation** with the steam having a positive charge and the water and metal boiler having a negative charge. The steam carries away the positive charge leaving the boiler negative.

v Wet steam, that is steam plus water, cannot be very highly charged as the negative charge in the water would neutralise the positive steam.

Pattinson was not too happy with his conclusions and speculated that some chemical activity might occur at the moment of generation of electricity.

2.2.5 Charles Schafhaeutl 1840 (24,25)

Schafhaeutl proposed that charge was produced by the condensation of steam to water droplets or spray as he had found that steam alone issuing from a jet did not produce electricity. He stated that it is only when water is present in the steam that electricity is produced. In a series of experiments in which he took account of the material dissolved in the water and forming incrustations on the boiler he stated that the quantity of electricity is not affected by the substances dissolved in the water. The steam cloud was always positive and the boiler negative.

Caught in a storm on Mt. Brenner (Tyrol), "having with me a barometer, thermometer, hygroscope and electroscope", he compared his steam experiment results with those of a thunderstorm.

He decided that violent winds caused condensation in the thunderclouds and generated the electricity discharged in the twenty one flashes he observed inside the cloud before his instruments were destroyed and from which he narrowly escaped with his life.

Schafhaeutl made the following comments on volcanic lightning, "It therefore appears that the column of vapour rising from the crater of a volcano seems to be in a similar condition to the fluttering steam issuing from the jet of Marcet's boiler, and the flashes of lightning attributable to separation of the liquid water from steam and smoke". Also, " it is obvious that the discharged electricity is owing to the expansion or condensation of the escaping water gas, if not to a chemical separation in the column of smoke ascending from the crater with an immense force".

Mention is also made of the fact that electricity is produced during the crystallization of certain salts.

2.2.6 John Williams 1841 (26)

Having studied meteorology for forty years, Williams set out to relate electricity from steam to atmospheric phenomena and volcanic lightning.

From repeatsof Volta's experiments he concluded that the positive steam cloud was charged, "on its immediate formation". Evaporation was decided upon as the source of charge and the decomposition of water was discounted. He stated that any source of water generated electricity though too weak to be detected.

To investigate volcanic lightning he insulated a portable furnace. He noted that the 'fumes' were negative and that the addition of fuel increased the amount of electricity," when smoke was dense just before bursting into flame". (A footnote clarifies that volcanic smoke is mainly steam mixed with,'di-electrics issuing from an orifice in non-conducting medium'.)

Investigation of steam from engines led to his invention of an apparatus very similar to Armstrong's generator and experiments with this device led him to conclude that, "Volcanic lightning is precisely analogous to the electric sparks given by effluent steam".

2.2.7 J.C.A. Peltier 1841 (27)

(This paper was located when the major part of my own investigation had been completed and it was of interest to note that Peltier had made some observations thought by the author to be original observations.)

Peltier attempted to explain the observations of Armstrong and Pattinson by results from his own studies of meteorology. He heated a sheet of platina to red heat and into a concave depression in the sheet he placed distilled water. The drop exhibited the Leidenfrost phenomenon though Peltier describes this in a way which indicates that he was unaware of the work of Leidenfrost some ninety years earlier. A drop which wetted the surface and evaporated produced no charge. A drop of salt water gave the same result and left salt on the metal surface. Each drop after the first became more concentrated, as it took up the salt left by the previous drop. He saw, 'minute bodies within the drop' and heard the sound of saline decrepitations accompanied by saline projections' and noted that his electrometer indicated a negative polarity. He stated that the vapour carried the charge away with it.

A very confused 'explanation' of his results follows in which some claim seems to be made for chemical decomposition producing charge. Armstrong's and Pattinson's results he explains as requiring saturated water and that electricity would only result when a saline coat was deposited in the boiler. (The minute bodies and sound of decrepitations observed by Peltier were items thought by the author to be original observations in the investigation presented in this thesis.)

2.2.8 M. Faraday 1843 (28)

In a series of ingenious experiments Michael Faraday investigated the electricity produced by steam escaping from an orifice. His conclusions, which for the most part demolished the ideas presented up to his time by others, were as follows :-

i The issue of steam alone does not evolve electricity (An observation made three years earlier by Schafhaeutl).

ii The electricity produced isnot due to either evaporation or condensation.

iii The electricity is due entirely to the friction of the particles of water which the steam carries forward against the surrounding solid matter of the passage.

iv Pure water must be used, any contamination, for example by salt, and no electricity is produced.

v The cause of the evolution of electricity by the liberation of confined steam is not evaporation but friction and therefore is not connected with the general electricity of the atmosphere.

2.2.9 S.H. Freeman 1882 (29)

Freeman seems to completely ignore Faraday's results and aimed to examine electricity produced by evaporation claiming that some work, not described, by Tait and Wanklyn made the results of Volta, Saussure and others of little value. He reached the conclusion, after dashing various solutions on to red hot platinum, that evaporation played little or no part in producing electricity. Despite Volta, he states, that evaporation contributed very little electricity to the atmosphere.

2.2.10 Concluding remarks, summary and some estimates of potentials involved in the investigations of 'steam electricity'.

Various sources of charge have been suggested down the centuries. The involvement of water and steam were recognised as possibly playing an important part in the production of volcanic lightning and it has been shown in this chapter that volcanoes have a variety of water sources

and chemicals which may also play a part in charge production. Important investigations of electricity evolved from the change in phase of water - steam - water were made during the 18th & 19th centuries. Apart from Freeman's paper of 1882 the feeling on the subject of 'steam electricity' seemed to be that Faraday had solved the problem. He had discovered that in the case of electricity evolved from boilers and jets the contact of steam transported water droplets with a solid surface was involved. The interesting search for an explanation had produced several discoveries not explained in Faraday's work but for reasons unknown to us today they were not taken up for further investigation and it may be that they were forgotten. There were four of particular interest:-

i Simple evaporation does not produce electricity.

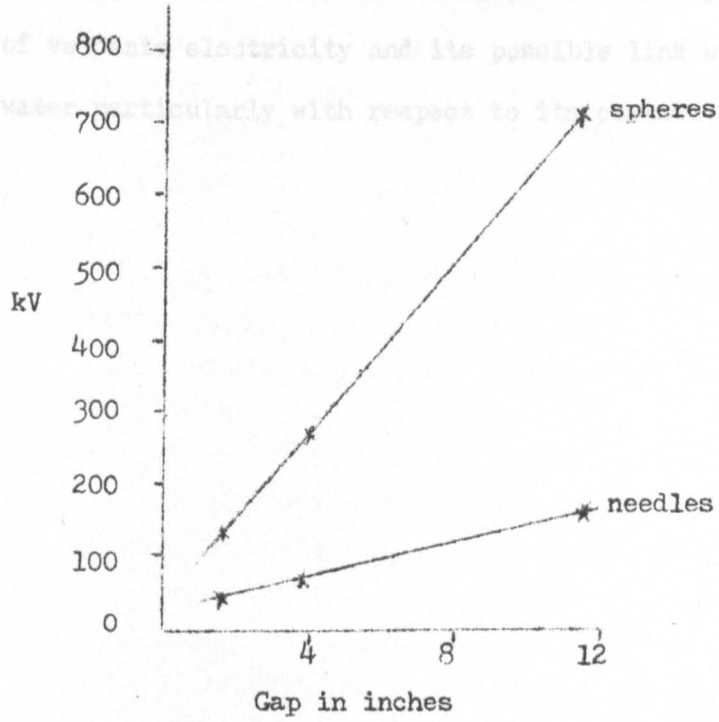
ii Ebullition or bubbling during evaporation produces electricity.

iii Aqueous solutions produce electricity when flash boiling on a hot surface.

iv Solution remaining stationary on the hot surface (the Leidenfrost phenomenon)does not produce electricity (Though Peltier seems to contradict this in the case of salt water).

Investigations of steam electricity were of a qualitative nature but Armstrong mentioned 4" sparks (2.2.3) as did Pattinson (2.2.4). In a recent paper by Anderson (1976) [30] dealing with the work of Pattinson and Armstrong on steam engines several spark lengths are mentioned and some idea of the shape of 'electrodes' may be gained viz. (a) shovel held in escaping steam with a penknife, held in the other hand, brought near to a boiler gave a 3/8" spark (Pattinson & Smith 1840). (b) Spark 2" long and corona from safety valve lever to brass cup surrounding valve (Armstrong & Nicholson 1840). (c) From rounded end of Armstrong generator boiler a 12" spark. Some rough estimates of potentials involved may be made on the assumption that the discharge 'electrodes', with one exception

(c), are sharp. Graph 1 shows the breakdown voltages between spheres or between needle points.



Graph 1 Applied voltage resulting in breakdown between (i) spheres 100 cm diameter, at N.T.P. (ii) needle points at 80 to 83% R.H. (From data in Electrical Engineers Reference Book 11th edition).

On the basis of the assumption made about electrode shape and bearing in mind that we are uncertain of the prevailing atmospheric conditions in the immediate vicinity of the experiments/observations - though it seems reasonable to assume conditions of high humidity due to the presence of steam - it is possible to state that the electric fields ranged in magnitude from 2.7×10^6 V m^{-1} maximum to 2.4×10^6 V m^{-1} assuming a spherical electrode configuration or, assuming needle point configuration, 9.9×10^5 V m^{-1} to 5.9×10^5 V m^{-1}. remembering the presence of steam, sharp edges and the observation of corona field values of 10^5 V m^{-1} would seem to be of a reasonable magnitude.

After about 120 years interest was in part renewed after a study of the steam clouds present in eruptions on Hawaii in 1950 and 1960 but more particularly in the emergence of Surtsey in 1963. Investigations of electrified clouds at Surtsey reopened the question of volcanic electricity and its possible link with evaporating sea water particularly with respect to its contact with heated surfaces.

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3.0.0 Saline solution on heated surfaces.

"As thikke as motes in the sonne-beem".

Chaucer, The Wife of Baths Tale.

The Times of Friday June 16th 1950 reported a haze which had existed in a belt 300 to 600 miles wide and 2,000 miles long over the Pacific Ocean. Its height over Wake Island was 16,000 ft and 7,000 ft over Hawaii where Mauna Loa had been in eruption since June 1st. The haze was attributed to steam clouds produced where white hot lava was running into the sea.

Ten years later, in 1960, Kilauea erupted and the haze was again observed. S. Price in a private communication to A.H. Woodcock and A.T. Spencer suggested that the haze could be made up of particles produced by the flash boiling of sea water in contact with lava.

3.1.0 Salt particles from sea water on molten lava. A.H. Woodcock and A.T. Spencer, 1961. (1)

Woodcock and Spencer wondered if such particles might be a source of raindrop nuclei and impactor samples were obtained on prepared slides. Little insoluble material was found, thus ruling out tephra, but hemispheres caused by droplets and what are referred to as 'moist particles' were found along with cubic salt crystals. An estimate of the particle weight distribution was made using the equation:

$$W = \frac{\pi}{6} D C g$$

where V = vol. of droplet $(\mu m)^3$

D = density of droplet gml^{-1}

C = conc. of salt by weight fraction

Flame photometer anlysis indicated that the samples contained sea salt. Laboratory experiments were made in which sea water was splashed on to heated lava, the ensuing cloud trapped in a metal cylinder and material allowed to settle on to glass slides.

The findings were that when sea water is splashed on to hot lava:- The average rate of particle production is about 2×10^{6} cm^{-2} s^{-1} and that the total weight of sea salt is 7×10^{-5} g cm^{-2} s^{-1} (when limited to particles of weight = 3×10^{-12}g). The size distribution ranged from 20 to 0.15 μm radius with the majority = 1 μm radius. Woodcock and Spencer felt that particles were produced in sufficient quantities to make the sea water/lava contact process relevant to meteorological situations.

3.2.0 Electrical charge from sea water on metal and lava. D.C.Blanchard 1964 (2).

As mentioned in the previous chapter observations at Surtsey (3) had revealed that material ejected from the crater was already electrically charged. Positively electrified clouds stated as possibly having 10^{5} to 10^{6} elementary charges cm^{-3} were produced where lava entered the sea.

Blanchard (2) cited the behaviour of saline solution put on a heated metal block viz. (i) At a block temperature below about 200° C a drop spread out quietly and evaporated in about one second with no current registered. (It should be noted that block temperatures were not measured but estimated from the tempering colour, of the oxide, coating.)(ii) When the block temperature was about 400° C or above a drop would move around on its own vapour (the Leidenfrost phenomenon) for several minutes and no current was observed. (iii) Between about 200° C and 400° C a drop bounced on the hot surface with a loud 'sizzling' noise and minute droplets of water were ejected from the block and negative current flowed. A chart record of noise, obtained by holding a microphone near to the drop, was compared with a chart record of current to show that maximum current flowed when noise was also at its maximum. (In this Blanchard confirmed de Saussure's observation made 178 years earlier).

Blanchard stated that charge separation per gram of sea water was found to vary with the one- half power of the water mass, ranging from about 400 e.s.u. g^{-1} to 40 e.s.u. g^{-1}. He assumed that an equal positive charge was carried off in the steam cloud, an assumption which could be checked by allowing the steam cloud to pass through a Faraday cage. He suggested that the charge was probably produced by the, "mechanical pulverisation of water" and that the findings of Woodcock and Spencer indicated this but, "in a manner not yet known, small droplets are torn from the bulk water during which process the drops become positively charged." Blanchard thought that double layer shearing might produce the charge, as he had found with bursting bubbles, but that no answer could be found until, "one understands the details of the mechanism by which the drops (i.e. droplets) are produced".

He went on to state that a 4.2 mm diameter sea water drop produced a cloud of volume 2,000 cm^3 approx with a charge of 15 e.s.u., having a mean density 2×10^6 as great as normal atmospheric positive space charge. Comparing this to a lava produced steam cloud Blanchard predicted that a cloud of 100 m radius would have a potential gradient of 10^6 V cm^{-1} falling off to 10^4 V cm^{-1} at a distance of 1 km (Normal weather gradient has a value of 1 V cm^{-1}). The predicted gradients would break down in discharges but space charge and gradient should still be high enough for easy measurement.

3.2.1 Combined work of Blanchard, Bjornsson and Spencer 1967 (4)

Conclusions reached from high frame speed films of sea water on heated lava and metal were that on lava at 1100° C a drop is suspended on its own vapour. At lower temperatures a drop spreads out and there is rapid evaporation during which bubbles and froths and droplets are flung off. In the case of a bouncing drop droplets seem to come from the water metal interface and it was assumed that particles were already dry salt when they struck the solid surface.

The conclusions reached by Woodcock and Spencer were assumed to apply and were used to estimate the charge on an individual particle on the basis that a drop of 3×10^{-2} cm^3 spreads out to cover 3 cm^2 and to evaporate in about 1 second producing 3×10^8 particles and a total charge of 1.5×10^{-10}C thus giving a value of 5×10^{-19}C per particle. Charge seemed to be inversely proportional to drop volume and more charge was produced from a rough surface than a smooth one. Chart records were not analysed but were thought to indicate that charge decreased with decreased salinity. Water from rivers draining the glaciers covering Katla and Grimsvotn was found to produce charge. Accidental organic contamination of a heated surface sometimes gave a reversal of polarity, an effect which ceased within a few minutes presumably due to heating. The suggestion was made, by Blanchard, that investigation was needed to find the relationship of particle size to charge as well as field work to study phreatic and sea water contact eruptions. No explanation could be given as to whether the particles originated as dry sea salt or as saline droplets but that the effect was possibly a surface mechanism.

Before making a summary of results it should be noted that there is one other paper, 'Water and the Generation of Volcanic Electricity' by Blanchard and Bjornsson (1967) [5] which is a descriptive work. The important details of the subject are contained in the papers reviewed here.

3.3.0 Summary of results.

(i) Woodcock and Spencer demonstrate the possible existance of salt particles produced when sea water is flash boiling on molten lava.

(ii) From impactor sampling and laboratory experiments they state that 2×10^6 particles cm^{-2} s^{-1} are produced by salt water flash boiling on a heated surface.

(iii) They state the range of particle sizes to be 0.15 to 20 μm radius with the majority less than 1 μm.

(iv) Particle weight was estimated to be 3×10^{-12}g.

(v) Blanchard discovered that at temperatures above that for quiet evaporation and below that for the Leidenfrost phenomenon a saline solution drop bounces and fragments producing charge and leaving the surface with a negative polarity. (In this thesis this phenomenon is referred to as the Blanchard effect).

(vi) On the assumption that a bouncing drop produced particles of the same size and in the same quantities as those stated by Woodcock and Spencer Blanchard stated an average charge per particle of 5×10^{-19} C.

(vii) Surface polarity may reverse from negative to positive when the surface is contaminated by organic material.

(viii) The opposite polarity of charge on the surface is assumed to be carried away on the steam cloud.

(ix) Blanchard suggested that the 'mechanical pulverisation', of water may produce the electrical charge and the particles are the residue of droplets 'torn off the drop in some unexplained manner'. But it was also suggested that the particles may be dry when they contact the hot surface and that a solid-solid contact charging mechanism might explain charge production.

(x) Decreased salinity will give decreased charge.

(xi) A volcanic steam cloud is predicted to have a potential gradient of 10^6 Vcm^{-1} falling off to 10^4 Vcm^{-1} which would break down in discharges.

3.3.1 A critique of investigations of saline solution on heated surfaces.

Although Woodcock and Spencer referred to a particle neither they nor the workers who later made use of their information actually describe a particle with respect to its mechanism of formation or to its structure. Several confusing terms are used,'round crystals', 'moist particles', but no detailed description of an actual particle.

That they were dealing with particles is not in dispute and the circular impressions on prepared slides certainly point to some kind of particle, or at least to a solution droplet from which a particle might form. Blanchard [6] was of the opinion that the hemispheres on the slides illustrated in Woodcock and Spencer's paper were due to water vapour condensing on to salt because of the humidity in the sedimentation chamber which was about 85% or 90%. He states that a salt solution crystallizes into a cubical structure or 'misshapen glob' from bursting bubbles.

From the author's own investigations, some details of which will be given in chapter 6, which included repeats of Woodcock and Spencer's laboratory work, it seems highly likely that any particles evolved, probably from droplets, would redisolve in the 'steam' and so revert to droplets and it is these droplets which are caught by impactor techniques as well as in the sedimentation chamber. Similarly in the Blanchard effect particles would revert to droplet form in the cloud of steam. In both instances particles may be detected and this will be shown to be the case in chapter 6 where particles from flash boiling, aerosol spray and Leidenfrost drops are compared in structure.

A disconcerting assumption was made by Blanchard and his co-workers with regard to obtaining an average charge per particle. It was assumed that the bouncing drop, that is in the Blanchard effect, was flash boiling on contact, as did water in Woodcock and Spencers work and that particles of the same size and in the same numbers were produced. This seems an unwise assumption as with the Blanchard effect many droplets can be seen to glide on the hot surface or be thrown clear of it whereas with flash boiling frothing ensues with many bubbles possibly producing more, smaller, particles and visual observation indicates various differences in behaviour to that seen in a bouncing fragmenting drop. The situation is ironical in that Blanchard discovered a phenomenon of boiling but reverted to what is arguably a different

form of boiling to obtain quantitative data. This matter will be pursued in chapter 10.

The Blanchard effect remains little investigated and two later brief papers, one by Pounder (1972)[7] and another by Sheldon (1974)[8] made a small contribution by verifying some of Blanchard's results with, in Pounder's work the confirmation, though only qualitatively, of the positive polarity of the cloud. Sheldon confirmed some of Pounder's, hence Blanchard's, results and attempted to determine dish temperature effects but with questionable graphical displays.

Particle structure, formation, production mechanism and charge distribution together with relationship between particle size and charge remain in need of investigation. (It will be remembered from chapter 2 (2.1.1) that it was the author's intention originally to present a study of the Blanchard effect and its associate charging process but a charging process associated with the Leidenfrost phenomenon was discovered and this became the investigation to be presented in this thesis. Thus the Blanchard effect remains for the most part unexplained and awaiting investigation.)

The comments of the critique should not detract from the contribution made to knowledge by the investigations discussed therein. By adding information to the embryonic subject of volcanic lightning they have also provided inspiration for further investigations. Several of the criticisms were made in one form or another by the 'pioneers' themselves.

Chapter 3 References.

1 A.H. Woodcock & A.T. Spencer, Lava - sea -air contact areas as sources of sea salt particles in the atmosphere,J. Geophysical Research, vol. 66,no.9, Sept. 1961

2 D.C. Blanchard,Charge separation from saline drops on hot surfaces, Nature, vol.201, no. 4925, pp 1164 - 1166,March 21 1964

3 Anderson et al, Electricity in volcanic clouds,Science, vol.148 no. 3674,May 1965

4 Blanchard, Bjornsson & Spencer, Charge generation due to contact of saline waters with molten lava, J.Geophysical Research, vol, 72, no.4, pp 1311 - 1323,Feb.1967

5 Blanchard & Bjornsson, Water and the generation of volcanic electricity,Monthly Weather Review,vol 95, no. 12,pp 895 -898 Dec. 1967

6 D.C. Blanchard, private communications 1974 - 1978

7 C. Pounder,Electrification from salt water on heated metals, J.Physics D, vol 5, 1972,pp 753 - 755

8 J.W. Sheldon,Charge separation from drops of Na Cl solution on a heated metal, J.Physics D, vol 7, 1974, pp L91 -L93.

4.0.0 The Leidenfrost Phenomenon.

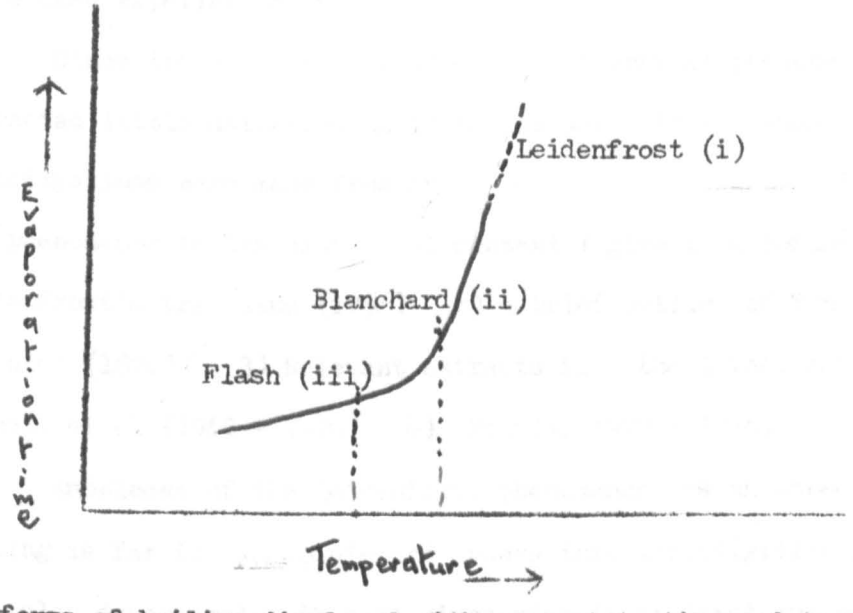
4.1.0 Introduction.

The Leidenfrost phenomenon occurs when a liquid (in this investigation water or aqueous solution) is placed on to a surface heated well above the boiling point of the liquid. It may be appropriate at this point to define forms of boiling as referred to in this investigation:-

(i) Leidenfrost boiling occurs when the liquid is lifted clear of the heated surface by a layer of vapour which is produced by the liquid in evaporation. It occurs at high surface temperatures and has long evaporation times.

(ii) Blanchard effect occurs at a lower temperature than that for (i) above and the liquid bounces and fragments into many tiny droplets which then exhibit Leidenfrost and flash boiling. Evaporation times are shorter than for Leidenfrost boiling but longer than for flash boiling.

(iii) Flash boiling is evident by the liquid spreading over and in contact with the heated surface and rapidly evaporating with considerable noise. It occurs at temperatures below that of (i) and (ii).



The forms of boiling displayed with respect to time and temperature.

In the Leidenfrost phenomenon the shape assumed by the liquid may be roughly spherical, disc like or irregular. The shape and dynamic behaviour may be affected by vapour bubbles. A drop may remain in one location or skim across the hot surface. It may spin, make fluttering noises, very rarely a musical note, or quietly evaporate. Evaporation times are surprisingly long in comparison to boiling by contact with the heated surface.

Any attempt to produce a hypothetical model of a Leidenfrost drop is fraught with the problems created by the unpredictable behaviour of each drop. An illustration of this is to be noted in attempts to determine the surface temperature at which a drop manifests the Leidenfrost phenomenon as distinct from other forms of boiling - the so called, "Leidenfrost Point". Bell's [19] survey of the American investigations of the Leidenfrost phenomenon reaches the conclusion that there is no unique value for this point for a liquid and that insufficient information is as yet available to make an a priori prediction on the probability of a stable drop, 'being established in any given case. One must either guess from the most similar experimental cases available, or, better yet, test one's case experimentally'.

Since its discovery in 1756 the Leidenfrost phenomenon attracted little attention until the decade 1960 -70 when some investigations were made from an engineering standpoint. To put the phenomenon in its historical context I give 1) a resumé of Leidenfrost's tractatus (1756) 2) a brief outline of Tyndall's lectures (1870) 3) Relevant extracts from the investigations of Bell et al (1960 - 1970) 4) Pounder 1970 - 1978) .

Knowledge of the Leidenfrost phenomenon as an aspect of boiling is far from complete and indeed this investigation into charged particles demonstrates that it gives rise to at least one other phenomenon.

4.1.1 J.G. Leidenfrost 1715 - 1794.

'Thou shalt separate the earth from the fire.'

Hermes Trismegistus.

In his 'Elementa Chemiae' (1732) Boerhaave [1] sought to establish chemistry as an independant science by excluding iatro-chemistry (Chemistry applied to medical theory - originated by Franciscus Sylvius (1614 - 1672) of Leyden [2]) He was inclined to favour the claims of the more celebrated alchemists and not to fully accept the phlogiston theory of G.E. Stahl (1660 - 1734). As Professor of medicine, botany and chemistry in Leyden Boerhaave influenced his pupil Johann Gottlob Leidenfrost who, although he did not concur with his teacher in all things, was biased towards alchemy.

In 1756 Leidenfrost was a medical doctor and lecturer in Duisburg, Germany where he published a 150 page, De Aquae Communis Nonnulis Qualitatibus Tractatus (A tract about some qualities of common water). The first part of the tract, translated by Wares and Bell (1966)[3], reviews the, 'nature of water, fire heat and the transformation of matter, from Thales to Boerhaave. Following this review is the section, 'On the fixation of water in diverse fire' and two sections,'Concerning the watery solid membranes of bubbles', and 'About the conversion of water into soot'. In the first of these he was the first to publish the fact that a soap bubble shrinks in size by expelling air through the tube which inflated it and proposed an early idea of surface tension to explain this.[4]

On the fixation of water in diverse fire.

Leidenfrost describes how distilled water was placed, via a glass tube, into a well polished iron spoon which had been heated to red heat in a fire. He noticed that the area where the drop first touched the spoon became dark, " as if the matter of light and fire from the glowing iron suddenly was snatched into the water".

A drop which had initially fragmented into smaller drops coalesced to form one shiny drop revealed, by carbon dust, to be spinning. A drop would take about half a minute to evaporate whereas on a cooler spoon a drop would take longer. The spoon would reach a lower temperature at which no drop formed and the water spread on the surface and rapidly evaporated.

Convinced that he had taken care to ensure that dust from the furnace had not entered the spoon led Leidenfrost to interpret the final stages in which the tiny drop made an audible, "Crack!" and left a fragment of solid in the spoon as being the conversion of water to earth in accordance with the formula :-

Fire + Water ⟶ Earth

He experimented with other liquids and suggested that the evaporation times of drops from heated surfaces would serve to measure temperatures in place of the cumbersome pyrometer invented by van Musschenbroek a short time before.

Two centuries after Leidenfrost the phenomenon which bears his name must be considered in fields as diverse as Cryogenics [5,6] Astrophysics and Cosmology [7,8]; Mass Spectrometry [9] and the temperature control of electronic devices. [10]

4.1.2 The demonstrations of John Tyndall 1863.

Tyndall [11] showed various aspects of the phenomenon by forming drops on the flattened base of a silver dish heated from below. He demonstrated the gap beneath a drop by placing a glowing platinum filament vertically behind it such that an observer could see part of the filament through the vapour layer. A simple circuit, suggested by Poggendorf, in which a battery in series with a galvanometer with one end of the circuit terminating in the drop and the other on the dish was used to show that the vapour layer apparently insulated the drop from the dish. On cooling the dish the drop made contact with it and a passage of current was indicated on the galvanometer.

The rosette manifested by some drops, and which Tyndall attributed to the regular escape of pulses of vapour, he projected on to the roof of the Royal Institution via a convex lens.

Garnett (1879)[12] explained the rosettes as being due to vibrations in the drop making it take the form of a curvilinear polygon, similar to the rim of a sounded bell, and that spark illumination revealed the rosette to be due to persistence of vision causing various positions of the polygon to be retained by the eye.

4.2.0 The American study of the Leidenfrost phenomenon (1960-1970)

As mentioned in the introduction (4.1.0) the study by Bell and others was made from an engineering standpoint. The interest was in the phenomenon as one aspect of boiling and how it related to modern technological situations such as rocket engines and cryogenic devices. The study may be considered in two sections (i) that of extended liquid masses (ii) liquid drops - the latter being most relevant to this investigation. It should be noted that the summary which follows is not exhaustive and is concerned only with material relevant to this thesis. Some of the terminology is perhaps more familiar to heat engineers and a note by way of clarification is first needed.

4.2.1 Terminology.

Zuber (1957) [13] defined three forms of boiling viz:-

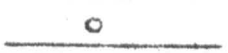
Film Boiling - occurs when the surface temperature is higher than for nucleate boiling and the liquid is wholly supported on a vapour layer or film. Heat flux is stated to be highest in nucleate boiling and least in film boiling. (This form approximates to Leidenfrost boiling (i) in the introduction).

Transition Boiling - occurs when the bubble population of nucleate boiling is great enough to constitute a vapour film or layer, described as being irregular and in violent motion. 'Transition' is a qualitative term used in papers up to Bell (1967) [19] where it is described as part nucleate and part film boiling. (It approximates to (ii)).

Nucleate Boiling - which occurs when a heated surface raises the temperature of a liquid in contact with it to a point at which bubbles of vapour form, or nucleate, on surface projections. An increase in temperature increases heat flux and bubble population. (It approximates to (iii),Flash boiling in the introduction.)

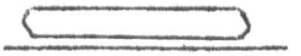
Zuber's definitions were made for large masses of liquid encountered in work with boilers. With respect to these definitions the definitions (i) to (iii) in the introduction to the chapter relate to similar phenomena involving small masses of liquid. A further definition may be made of the so called Leidenfrost Point of a liquid - it is the temperature at which the liquid changes regime from nucleate/flash boiling to stable film boiling i.e. exhibits the Leidenfrost phenomenon and at which total evaporation time is maximum and heat flux minimum.

Fig.1 (from Bell (1967) illustrates the outline of different volumes of liquids undergoing film/Leidenfrost boiling.



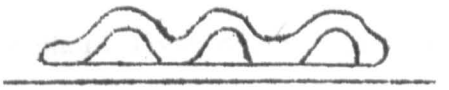
(a) Small drop spherical

(b) Large drop flattened sphere



(c) Extended drop Flat disc,thickness constant

(d) Extended drop Flat disc,thickness constant, single bubble breakthrough



(e) Extended drop,Flat disc, thickness constant, multibubble breakthrough. (I do not agree with this description with respect to, 'flat disc' the drop changes shape as bubbles burst).

4.2.2 Conclusions reached in the investigations of 1960 -1970.

4.2.3 Instability and bubble breakthrough.

These conclusions are taken from papers by, Zuber (1957)[13], Berenson (1961)[14], Hostler and Westwater (1962)[15], Godleski and Bell (1962)[16], Gottfried, Lee and Bell (1962)[17], Patel and Bell (1966)[18], Bell (1967)[19], Rhodes and Bell (1966)[20], and Keshock and Bell (1970)[21] dealing with investigations of liquids as drops or as extended masses with bubble breakthrough (see Fig.1) involving water, binary solutions, freon and liquid nitrogen. There is considerable repetition of material in the papers, a problem allieviated by Bell's survey of 1967 (ref.19) .

The Leidenfrost phenomenon presents a temporary situation in which one fluid is supported by one of less density as long as energy is fed in to maintain the vapour layer. Taylor (1949)[22] considered the instability of the lower surface of a more dense fluid at the interface of two fluids. A disturbance on this surface, Taylor proposed, would increase exponentially so long as amplitude was small in comparison to wavelength with the rate of development of the instability being proportional to:-

$$\sqrt{\frac{\rho_2 - \rho_1}{\rho_2 + \rho_1}}$$

where ρ_1, ρ_2 are densities of the two fluids.

Investigations in which attention was paid to Taylor instability reached the conclusions that:-

(i) Disturbances of short wavelength are short lived due to surface tension (γ) which restores the smooth interface.

(ii) There exists a critical wavelength (λ_c)

$$\lambda_c = 2\pi \left[\frac{\gamma}{g(\rho_l - \rho_v)} \right]^{\frac{1}{2}}$$

where γ surface tension

ρ_l density liquid

ρ_v density vapour

g gravitational acceleration

at which large disturbances are not damped out but which can only exist on surfaces having some linear dimension comparable to the wavelength.

(iii) It was found that a wavelength λ_d, called the "most dangerous", grew most rapidly as an instability:

$$\lambda_d = 2\pi \left[\frac{3\gamma}{g(\rho_l - \rho_v)} \right]^{\frac{1}{2}} = 1.732\,\lambda_c$$

Leidenfrost boiling instability is revealed by bubbles breaking through the upper surface. Results from the study of large masses of liquid (Hostler & Westwater [15]), confirm instability theory. Patel and Bell [18] citing the earlier work of Borishansky and Kutateladze (1953) state that the smallest water mass in which bubbles were observed to break through was 2.8 ml and the largest mass observed without bubbles was 5.8 ml but no surface temperatures are given.

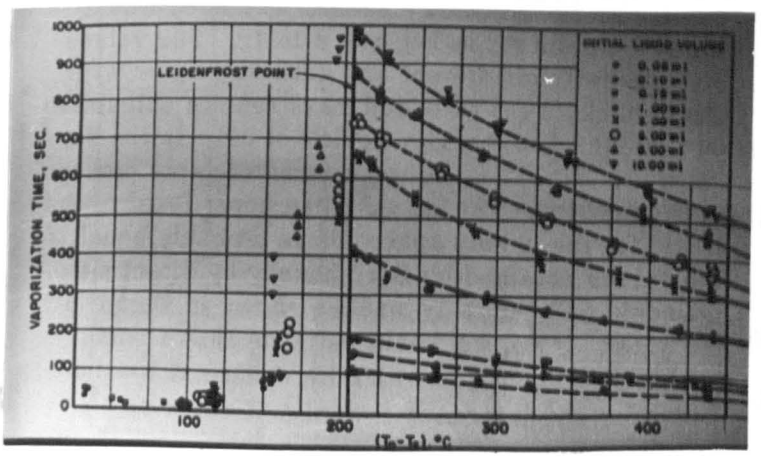
Since the author confined the study of the phenomenon of particle emission to solution drops having a mass of 1 ml further detail of bubble breakthrough and instability with extended masses would be out of place here. It has been necessary to present a brief outline both to indicate its existance as well as to be aware of bubble breakthrough in evaporation time studies.

4.2.4 The Leidenfrost point and evaporation times.

The leidenfrost point as defined by Bell et al [17,19], is the onset of stable film boiling at the plate temperature at which evaporation time is greatest. No precise Leidenfrost point could be determined for water and it was given as a range from 250°C to 310°C (plate temperature). It was found that the mass of water used did not affect these values but several factors seemed to be responsible for the difficulties encountered in attempting to determine the Leidenfrost point: - (i) Surface roughness - Bradfield (1966) cited by Bell, observed surface liquid contact on aluminium with a root mean

square roughness of 70 μm with, 'occasional mesa like protruberances about 10^{-3} in high'. (ii) Mode of deposition of the liquid - it was found that an individual could obtain consistent results whereas others using the same apparatus, ' may consistently disagree'. Stating that there is no apparent way to quantify this factor empirical note is taken that 'liquid poured with a sideways motion' was most likely to produce a stable drop than liquid dropped on to the surface. The reason for this, it was suggested, would be in the minimisation of normal velocity to the vapour layer in a sideways moving drop so reducing the possibility of destroying the layer. (iii) A surface perturbation, e.g. ripple, introduces a velocity component normal to the vapour layer and may cause surface contact. When this happens the cooled area may not reach its former temperature fast enough before a second perturbation causes the liquid to wet the surface and the stability be destroyed. (Consequently the thermal conductivity of the surface is important.) Bell's conclusions on the attempts to determine the Leidenfrost point were given in the introduction to this chapter (4.1.0).

Fig. 2 shows the evaporation time to surface temperature for various volumes of water.



At the lower surface temperatures, 170°C to 200°C, the water wets the hot surface and nucleate/flash boiling occurs with rapid evaporation. At temperatures from about 200° C to 300° C evaporation times increase due to a change to part nucleate, part film boiling (Bell - so called transition boiling). Maximum evaporation time is reached at about 300° C at which stable film boiling is attained (see Leidenfrost point above). Beyond the Leidenfrost point evaporation times gradually decrease with increasing plate surface temperature.

Bell [19] points out that knowledge on the evaporation from the upper surface is non - existant and information on the behaviour of the vapour from the underside of the drop is also lacking. Does the vapour escape in a horizontal laminar flow or does it rise up and enshroud the drop ?

Keshock and Bell [21] suggested that liquid nitrogen, having a lower surface tension than liquids previously used in studies of the Leidenfrost phenomenon, makes it possible to study the effect of vapour breakthrough on the evaporation time and claim that heat transfer is increased to extended masses by vapour breakthrough.

Comments on some assumptions made for 4.2.4.

(a) It was assumed that a drop surface is smooth (In fact observations reveal ripples over the surface which is also subject to unpredicatable disturbances).

(b) The assumptions were made that heat travels to the base of the drop by conduction through the vapour layer and radiant heat is ignored as only being likely at high surface temperatures (no value given) and that heat to the upper surface may be ignored except for small spheroids when radiant heat may reach the upper region.

(c) It was assumed that water mass is removed by evaporation into the vapour layer. No attempts were made to obtain information on its behaviour either in the layer or on leaving it.

(d) Baumeister [23] assumed that vapour from the layer rose and

and enshrouded the drop and that mass removed from the upper surface is by diffusion into the inert atmosphere above the drop. (The atmosphere above the drop is never 'inert' as convection currents are in evidence - by shining a bright light above the drop and observing the familiar 'heat waves', due to varying air density, on a white screen placed behind it - thus heat will be convected to the sides and possibly the upper surface of the drop.)

Godleski and Bell [16] describe the behaviour of evaporating drops as forming a flattened biscuit shaped pulsating drop when first placed on the hot surface. The pulsations occur at the rate of about 1 per second with the rate increasing as the drop diminished in size until the drop finally becomes a blur. The now small drop is spherical and if a tiny bubble exists inside it will be whirled violently within the drop. Sometimes the drop bounces to a height of five or six times its own diameter. Drops constantly move about, usually following a circular path at speeds up to about 30 cm s^{-1} with occasional changes in direction. (A circular path would only be taken by a drop in a spherical dish and such a course seems unlikely on a flat plate as used by Bell et al). (This is a generalised account as it is not possible to state what a particular drop will do.)

The rosette is not mentioned in these investigations and neither are the sounds attendant with an evaporating drop. The bouncing drop, described above, is in the author's experience a somewhat rare occurrence; certainly more rare than the rosette.

4.2.5 The thickness of the vapour layer.

Gottfried, Lee and Bell [17] mention an earlier report by Kistemaker (1963) in which he used x - rays to measure the vapour layer thickness beneath a barium loaded drop of 0.05 ml volume (water) on a surface at 500°C and found it to have a mean value of 0.006 cm. The failure of a photographic attempt to measure the layer thickness, by Gorton (1953), is also mentioned but without details.

4.3.0 Some studies of the Leidenfrost phenomenon undertaken for this investigation 1972 - 1978.

4.3.1 Observations of drop behaviour.

(The material of this section is confined to the observation of distilled water though certain liquids viz ether and methylated spirits examined in a diversion from the main body of the investigation display the same behaviour.)

Information gathered during observation of many hundreds of drops make it possible to classify drop activities as being standard or anomalous as well as to explain some of them. In the course of the investigation photography has been used in addition to observation by naked eye and reading telescope. Photographs of drops were obtained using a single lens reflex camera type Minolta SRT 303 with extension tubes and flash bulbs type PF1B, or light from a slide projector. Ilford 35 mm film type FP4 (125 ASA) or HP4 (400ASA), was used and processed in Acutol or Acuspeed and Acufix. Naked eye and reading telescope (magnification 8x) observations were made variously in daylight, sunlight or projector light.

Standard behaviour.

Drops of about 4 ml and above will have a changing geometrical outline and large vapour domes will appear (Fig.1 (e)) some of which will break through the upper surface of the drop. The thickness of the drop will be the same for volumes above about 2 ml; any increase in volume giving rise to an increase in area in preference to an increase in thickness. When the drop has diminished to about 3 ml from any initial volume there will be a single vapour dome or bubble (Fig.1(d)) as shown in photograph 1. Photograph 1 shows a 3/4 view of a Leidenfrost drop revealing the irregular outline of the drop body, the vapour dome - the top of which is apparent as a white disc of reflected light - and the inner walls of the dome. The dotted background is the brass heated surface.

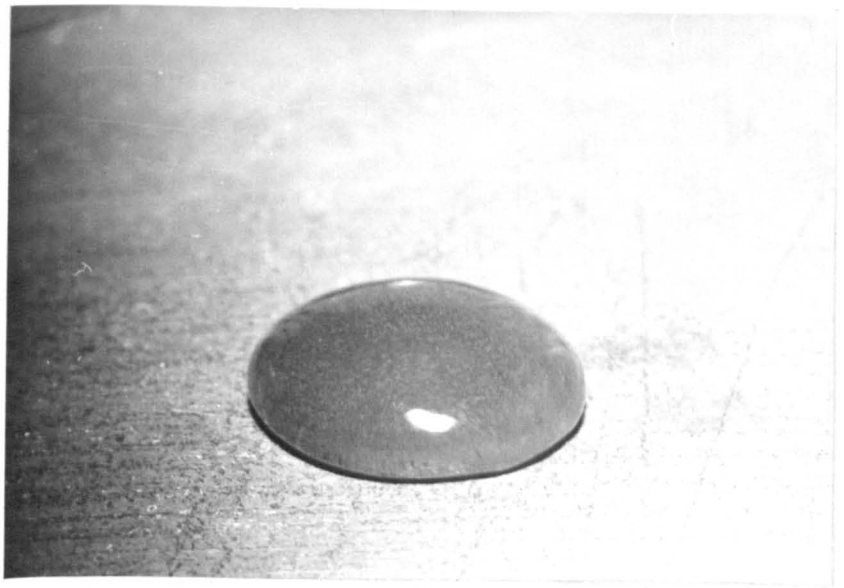
Photograph 1 1/500 s.

The outline will continue to change. On reaching a volume of 2.8 ml (approx), it will be observed that the vapour no longer forms a thin roofed dome or bubble but that it now has a thicker roof and no longer breaks through the upper surface of the drop. The drop is now similar in shape to a concavo - convex lens, convex side uppermost. As volume is further reduced, by evaporation, the outline will become elliptical or circular. At volumes below approximately 0.25 ml the drop is a flat bottomed sphere (Fig.1 (b)) ultimately becoming spherical at volumes of about 0.05 ml (Fig.1(a)). It will completely evaporate and if it has collected any oxide or solid matter it will make a distinctly audible, "Crack!" and the oxide will remain on the surface (see Leidenfrost 4.1.2 for the original observation). Drops below the volume at which vapour bubbles no longer break the upper surface have currents, made visible by a fragment of balsa wood carbon/ charcoal, which traverse the underside of the drop, move over the upper surface and back across the underside.

Anomalous behaviour.

Noises :- A large drop with vapour breaking through may make fluttering noises particularly if the drop is broken apart by a bursting bubble - it will coalesce again. A drop displaying a rosette sometimes makes a sound similar to the flicking over of the pages of a book. On very rare occasions drops less than about 2.8 ml make a musical note at about C (256 Hz).

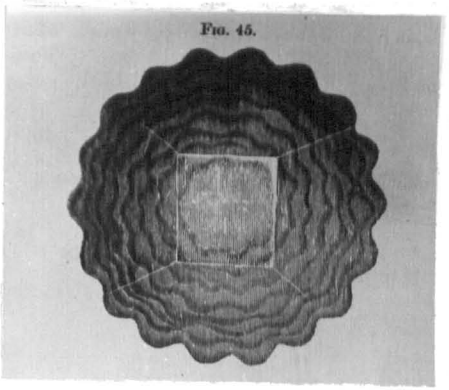
A drop may remain in one location until evaporation is complete or it may skim across the heated surface. It may suddenly change its direction of motion. The drop surface may be smooth, as in photograph 2, or waves and ripples may appear (this is most likely) as in photographs 5 and 6.



Photograph 2 1/250 s

The granulated appearance is due to the drop acting as a lens and magnifying the brass, hot surface. The white mark is reflected flash.

An outline having aesthetic appeal, and named by Tyndall the rosette, is an optical illusion (see Garnett 4.1.3). Photograph 3 is taken from a drawing in Tyndall's book,'Heat a mode of motion' (11).



Photograph 3

A photograph of a drop displaying such a rosette (Photograph 4 taken at 1/250 s), confirms Garnett's observation.

Photograph 4 1/250s

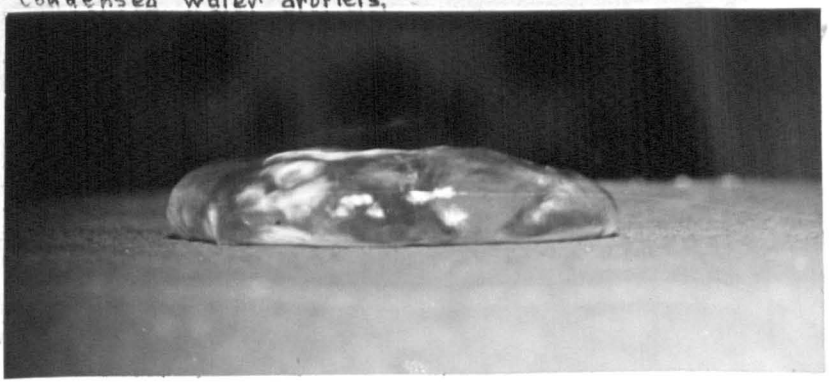
In this case i.e. photograph 4 the rosette resulted from a three pointed pulsating drop. Other photographs of rosettes have revealed an elliptical drop from 'rosettes' having less petals, confirming Garnett's idea of a curvilinear polygon.

Some drops in the final seconds of evaporation exhibit concentric rings of waves which appear to originate in the centre and travel outwards and downwards. The drop may suddenly jump upwards and fall back to bounce on the surface and it may continue this behaviour

until evaporation is complete.

The Vapour:-

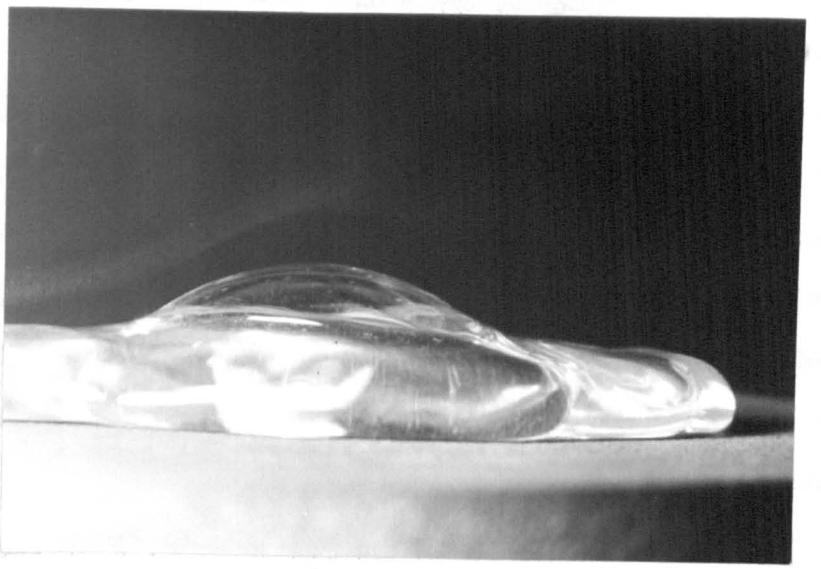
Bell (4.2.4) stated that knowledge on the behaviour of the vapour escaping from the drop supporting layer was non-existant and asked the question, "Does it rise up and enshroud the drop ?" Careful examination of photographs 5, 6 and 7 shows 'steam' appearing to 'enshroud' the upper surface of the drop. This is particularly noticeable in photograph 7 in which it will be seen that the 'steam' (of condensed droplets), to the left of the photograph, actually takes on the outline contour of the drop in that it is horizontal above the liquid and rises up and over the vapour dome. This implies that evaporation may be less from the upper surface and greater from the lower, nearest to the heat source. Evaporation from the lower surface will be into the vapour layer from which vapour may then rise up and over the drop, condense, and appear as a 'steam' of condensed water droplets.



Photograph 5 1/500s A side view of a drop on a heated brass surface. Notice the irregular surface features amd the upturned bottom edges of the drop. Steam may be seen over the top - left to middle - surface.

Photograph 6 is a side view of a drop. The surface features are much in evidence as well as the lower edge and 'steam' above the upper surface. Waves are travelling over this drop giving it an uneven thickness.

Photograph 6 1/500s



Photograph 7 1/1000s A side view of a large drop showing a vapour dome, 'enshrouding' steam - left up and over dome - and upturned lower edge.

4.3.2 Behaviour of some aqueous solutions exhibiting the Leidenfrost Phenomenon.

The substance most used as the solute was Na Cl beacuse the investigation evolved from the earlier work of Blanchard et al on saline contact charging; work which itself originated in the analysis of the emergence of Surtsey (chapters 1 & 3). Salt may not always be the predominant solute (see chapter 2) and for this reason some

attention has been paid to other substances capable of forming an aqueous solution. (Samples of thermal spring water were also used.) Saline drops were of 3.5 % concentration Na Cl, which is the predominant solute in the world's seas and oceans which have an average salinity of 3.5% though particular salinities may be as high as 19.2% ,Dead Sea, or as low as 0.72%, Baltic Sea, (Holmes [24]).

The behaviour previously related for water drops (4.3.1) was found to apply also to drops of aqueous solution but with an exception of major importance :

4.3.3 Production of a charged particulate cloud from solution drops exhibiting the Leidenfrost phenomenon.

During the observation of a drop formed from 3.5% Na $Cl_{(aq)}$ the drop was diminishing in size when suddenly it made a distinctly audible, "Crack!" The drop appeared to break apart but to quickly reconstitute itself and then continue to quietly evaporate. However the same phenomenon again occurred and continued to do so more frequently until the drop had completely evaporated leaving only a small salt remnant on the heated surface. Observation of more salt drops showed that this behaviour occurred each time and that the phenomenon was therefore reproducible. It was further noticed that on the heated surface small spherical pieces of salt were present in addition to the larger remnant from the drop. A probe connected to an electrometer, the full details of which will be given in chapter 7, was located in the drop and each time the now familiar sound was heard charge was registered. In addition to the larger spherical salt pieces on the heated surface many small specks or particles were detected, in a projector light beam which happened to be on at the time, in the air of the room containing the apparatus.

A search of literature indicated that this behaviour of aqueous solution drops exhibiting the Leidenfrost phenomenon may be a new phenomenon. Peltier (1841) had observed decrepitations accompanied by

charge but had not followed up his observations (2.2.7).

It was found that other solutions generated charge in this way and more details will be given of exploratory work on these in chapter 8.

This chance discovery of some particle emitting charging process associated with the Leidenfrost phenomenon thus became the main object of study in this investigation.

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5.0.0 Evaporation of Leidenfrost drops.

5.1.1 Drop volume and total evaporation time.

The temperature of a stainless steel dish placed on an electric boilng ring was measured using a Chrome/Alumel couple connected to a Kelvin and Hughes pyrometer (0°C to 1200°C, 9" mirror scale).

Dish temperature = 610 °C

Drop volumes ranging from 10 ml to 5μl were measured into the heated dish from hypodermic syringes and micro - pipettes. The time taken to complete evaporation of each particualr volume was measured with a hand triggered Dekatron timing unit (Butler Radio Ltd., Rochester, type 1350A), For the purposes of investigating the charging phenomenon associated with Leidenfrost boiling (4.3.3) a volume of 1 ml was considered to be of reasonable size for study and free from disturbance due to vapour breakthrough. It is unfortunate that the graph published by Patel and Bell (Fig.2, 4.2.4) of evaporation times of different volumes is so small and so lacking in detail that accurate extrapolation is impossible. However sketching in extrapolated curves from 450°C and comparing drop volume to time (v,t) at 610°C there is reasonable agreement. The evaporation times for drops of volume 1 ml (1,000μl) to 0.30 ml (30μl) are displayed in Fig.1 and those for volumes ranging from 0.04ml (40μl) to 0.005ml (5μ l) are displayed in Fig.2

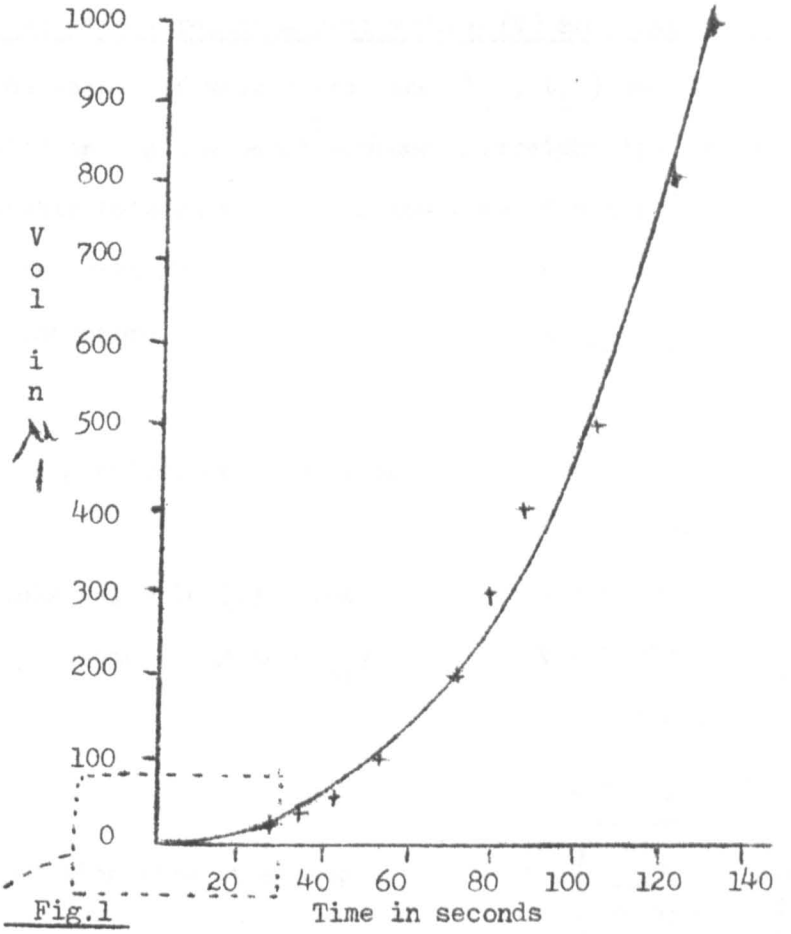

1000
900
800
700
600
500
400
300
200
100
0
Vol in
20
40
60
80
100
120
140
Time in seconds

Fig.1

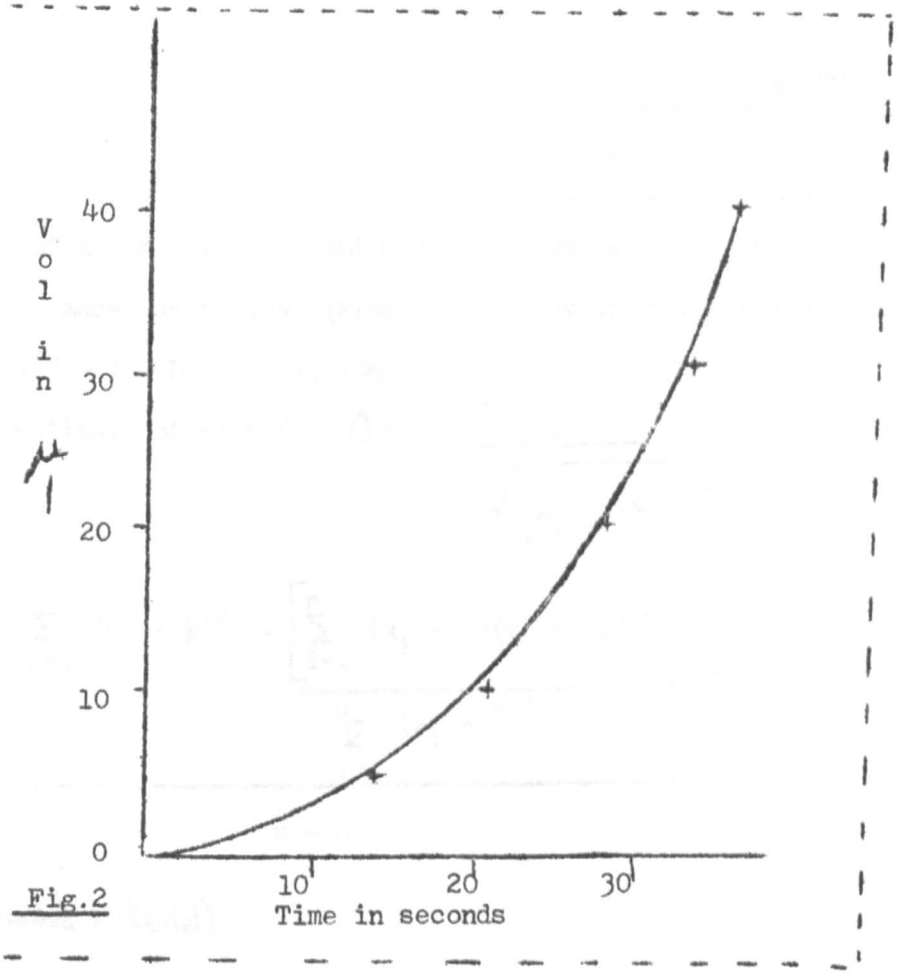

40
30
20
10
0
Vol in
10
20
30
Time in seconds

Fig.2

Empirical equations relating drop volume (V) and total evaporation time(t)

The values of volume and time (V_i , t_i) used to obtain Figs 1 & 2 when plotted on log log paper* produce a straight line which indicates a relationship between V and t of the form $V = a\, t^{n}$ -------(1)

From the straight line $n = 2.4$

Therefore $a = \dfrac{V}{t^{2.4}}$ ------(2)

Substituting values of V and t in (2)

$a = 0.0074$

putting this value in (1) gives $V = 0.0074\, t^{2.4}$ --(3)

hence drop volume (3.5% $Na\,Cl_{aq}$) $V = 0.0074\, t^{2.4}$ μl

$= 7.4 \times 10^{-3}\, t^{2.4}$ μl

$= 7.4 \times 10^{-9} t^{2.4}$ l --(4)

Total evaporation time of a drop $t = \left(\dfrac{V}{0.0074}\right)^{\frac{1}{2.4}}$ s ---(5) (V in μl)

$= \left(\dfrac{V}{7.4 \times 10^{-9}}\right)^{\frac{1}{2.4}}$ s ---(6) (V in l)

The values of n and a will be subject to errors and some estimate of these may be made as follows (From Menzel,Fundamental formulas of Physics. vol.1, pp 118 - 119 Dover,N.Y. 1960)

s.d. of estimate of slope(n) $\Delta n = \dfrac{s}{\sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2}}$ ---(7)

where $s = \sqrt{\dfrac{\sum_{i=1}^{n} (y_i - \bar{y})^2 - \left[\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y})\right]^2 \Big/ \sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 2}}$ -------(8)

* (see Appended Material).

Values of volume and time placed into (8) and (7) gives an estimated error on n of $\pm$ 0.3

so that $n = 2.4 \pm 0.3$

The estimated s.d. error on a $s_a = (s)\sqrt{\frac{1}{n} + \frac{\bar{x}^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2}}$ --(9)

$= \pm 0.0003$

so that $a = 0.0074 \pm 0.0003$

We thus find that the curve is fitted by

$V = at^n$ where $a = (7.4 \pm 0.3)\ 10^{-3}$

(or $t = \left(\frac{V}{a}\right)^{\frac{1}{n}}$) $n = 2.4 \pm 0.3$

5.1.2 The Vapour Layer.

Pressure in the vapour layer.

Pressure $P = \frac{\text{Force}}{\text{Area}}$

if Force F = Mass m x Acceleration due to gravity (g)

and Mass m = Volume V x Density D

then $F = V\ D\ g$

Assuming that the density of 3.5% Na Cl_{aq} solution is the same as for water then $D = 10^3$ kg m^{-3}

and since $g = 9.8$ m s^{-2}

then $P = \frac{V \times 10^3 \times 9.8}{A}$ -------- (10)

where V = drop volume m^3

A = Area of drop base m^2

In order to continue further it is necessary to have some means whereby the area of the drop base may be determined from the drop volume.

Area of drop base with respect to drop volume.

A sheet of plain glass was carefully coated with a layer of vaseline on one side. By passing this surface to and fro above a spirit flame the surface was made smooth. A new glass tuberculin hypodermic syringe was used to deposit drops on the vaselined surface on the glass placed on mm squared paper. Area was measured by the method of counting squares observed through a reading glass. Very small drops below about 0.02 ml are difficult to measure due to distortion of the lines on the paper as the drop acts as a small lens. Drops above about 2 ml spread due to their weight but since this investigation is concerned with drops of a less volume than this the spreading of larger volumes is irrelevant. The areas for twenty different volumes were determined from which the graph in Fig. 3 was produced. (Volumes up to 3ml have been used to extrapolate the graph further than in Fig.3 and have shown it to be reliable up to about 2ml. Since this investigation has used drops having an initial volume of 1 ml which reduce, by evaporation, to less than 0.6ml by the time base area needs to be calculated the range covered by the graph of drop volume to area of drop base (Fig.3) was considered suitable.

The relationship of drop volume to drop base area is of the form

$$\text{Area } A = k\,(V)\ \text{Volume} + C$$

and since $C = 0$

then $A = k\,V$

substituting values for A and V

gives $k = \frac{A}{V} = 190$

therefore $\underline{A = 190\,V}$ ----(11) where $A = m^2$

$V = m^3$

The error on k (=190)

s.d. of estimate of slope $s_b = \dfrac{s}{\sqrt{\sum_{i=1}^{n} x_i^2}}$

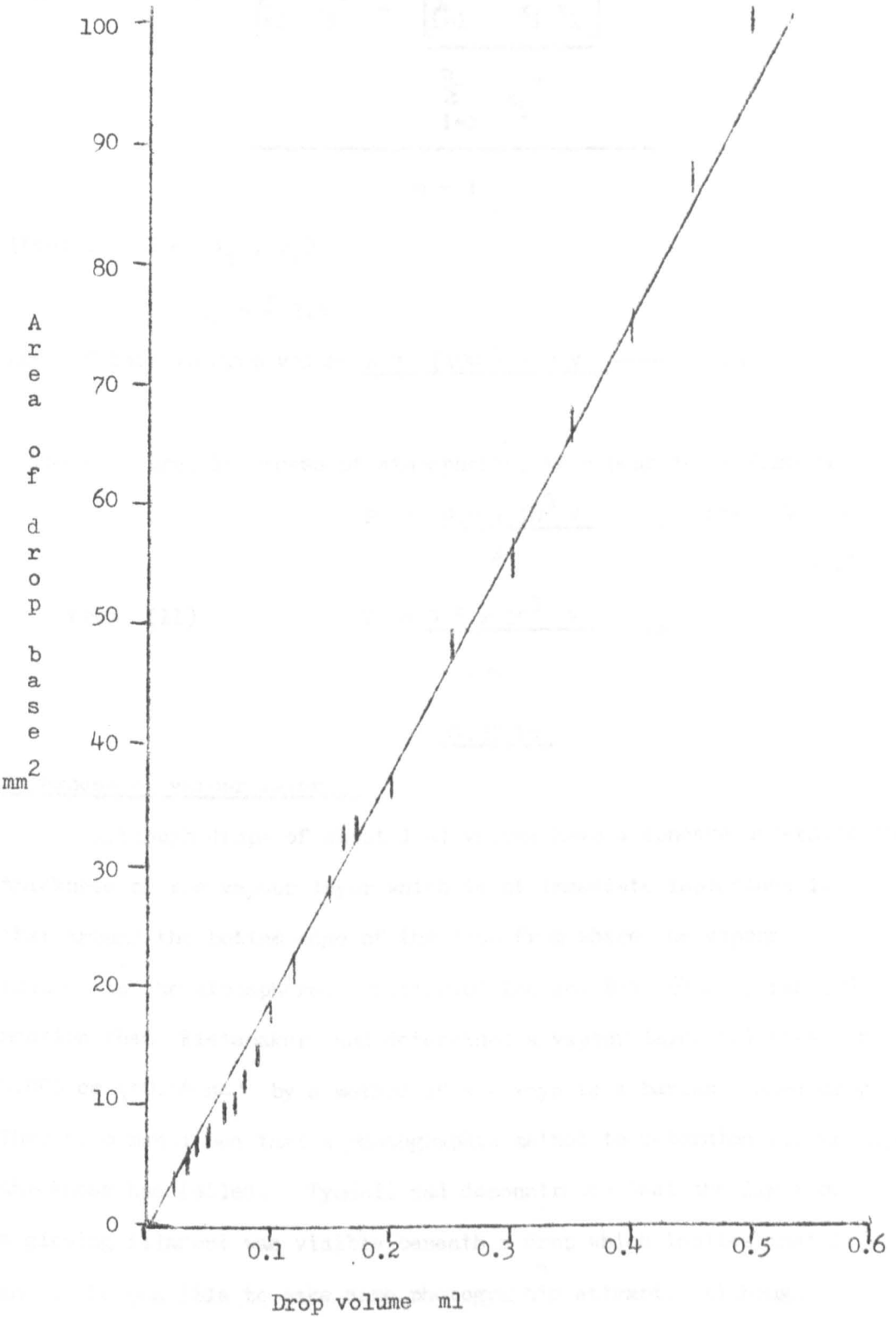


Fig.3 Drop volume to area of base exposed to hot surface.

(For drop volumes up to about 2ml extrapolation is reliable - and has been tested experimentally - above 2ml the drop spreads and the graph thus becomes unreliable.) (See text).

where $$s = \frac{\sum_{i=1}^{n} y_i^2 - \frac{\left[\sum_{i=1}^{n} x_i y_i\right]^2}{\sum_{i=1}^{n} x_i^2}}{n-1}$$

(from 10 values x_i , y_i)

$$s_b = \pm 3.5$$

Area of base to drop volume $A = (190 \pm 4)\, V$ -------(12)

The pressure, in excess of atmospheric, in vapour layer (from 10)

$$P = \frac{9.8 \times 10^3\, V}{A} \text{ Pa} \qquad \text{where } V = m^3, \; A = m^2$$

from (11) $$P = \frac{9.8 \times 10^3\, V}{190} \text{ Pa}$$

$$= 51.57 \text{ Pa}$$

Thickness of vapour layer.

Although drops of about 1 ml volume have a concave underside the thickness of the vapour layer which is of immediate importance is that around the bottom edge of the drop from where the vapour escapes to the atmosphere. Gottfried, Lee and Bell (4.2.5. ref 17) mention that Kistemaker had determined a vapour layer thickness of 0.006 cm (=0.06 mm) by a method of x - rays to a barium loaded drop. They also mentioned that a photographic method to determine vapour layer thickness had failed. Tyndall had demonstrated that the light of a glowing filament was visible beneath a drop which implies that it should be possible to make some photographic attempt. Although Photographs 6 & 7 of chapter 4 had been taken only with the view to illustrating some features of Leidenfrost drops they provided a means whereby the thickness of the edge of the vapour layer might be measured.

When enlarged prints* were made it was possible to measure the gap between the bottom edge of the drop and the heated surface to reveal that it was 0.06mm for most of the length of the drop edge except in two places where the edge appeared to curve upwards at which places the gap was 0.26 mm. These two places are at the 'end' of each drop and may be either the change in geometry of shape or, though less likely, due to a ripple passing over the drop surface.

By photography then it seems reasonable to state that the vapour layer thickness at the edge of drops on a surface at 610°C = 0.06 mm.

5.1.3 The flow of vapour from the supporting layer considered as the escape of a fluid from an orifice.

The rate of escape of a fluid from an orifice is goverened by the geometrical shape of the orifice and the area of discharge. The coefficient of discharge (C_d) is not constant, depending on Reynolds number, area of orifice and to some extent on the orifice shape - which affect the coefficient of velocity (C_v) to which the coefficient of discharge is related by:-

$$C_d = C_v \times C_c$$

where C_v is the coefficient of velocity which is the ratio of actual mean velocity in the cross-section of the stream jet to the ideal mean velocity if friction were not present. C_c is the coefficient of contraction which is the ratio of the area of the contracted section of the jet to the area of the opening through which the liquid flows. (From Fluid Mechanics and Hydraulics by R.V. Giles, 2nd edition, Schaum, New York.)

Values of C_d exist for large scale hydraulic engineering for pipes, reservoir discharges and on the smaller scale for Venturi meters. Unfortunately information is limited. Medaugh & Johnson tabulate values for water at 60°F discharging from a vertical sharp edged circular orifice with C_d values ranging from 0.647 to 0.593.

*(see Appended Material)

A value of C_d of 0.665 was located and used in the exploratory work on vapour flow from the vapour layer, conducted prior to the location of Cd values tabulated by Meddugh & Johnson.

Assumptions made in considering the vapour layer under Leidenfrost drops.

(i) That the orifice is of constant area.

(ii) That the structure of the orifice is sharp edged - in order to use published C_d values.

(iii) That the evaporation in the main is into the vapour layer and if so then the rate of flow will be identical to the evaporation rate to be determined from the graph of total evaporation (section5.1.1)

$$\text{Flow } Q = C_d A_o \sqrt{\frac{2 (p1 - p2)}{\rho}} \quad \text{------(13)}$$

where ρ = density of vapour assumed to be that of air i.e. 1 kg m^{-3}

$(p1 - p2)$ = pressure excess in vapour layer = 51.57 Pa

A_o = area of orifice

Area of orifice A_o

Considering the orifice area to be the walls of a cylinder

then $A_o = 2\pi r d$ ---------(14) where r = radius of base of drop (obtained from area of base).

d = thickness of vapour layer i.e. gap between base of drop and heated surface.

Several values may be determined for A_o using values of r obtained from various base areas (12) for different drop volumes. Hence using equations (14) and (13), in that order, values of Q for several drop volumes of 3.5% Na Cl_{aq} aqueous solution $\leq$ 1 ml have been calculated and listed in Table 1.

Table 1 Vapour flow rate ml s^{-1}

C_d = 0.665 d = 0.06 mm

Volume ml	Q ml s^{-1}
1.0	0.019
0.9	0.018
0.8	0.017
0.7	0.016
0.6	0.015
0.5	0.014
0.4	0.012
0.3	0.011
0.2	0.009
0.1	0.006

Comparison of flow rate of escaping vapour from layer with evaporation rate.

Drop volume (V) to total evaporation time (t), where V is in ml for comparison with Q ml s^{-1}, is $V = 0.007\ t^{2.4} \times 10^{-3}$ ml.

Therefore evaporation rate $\frac{dV}{dt} = 1.68\ t^{1.4} \times 10^{-5}$ ml s^{-1} --(15)

Since total evaporation time may be calculated from (6) and dV/dt from (15) evaporation rates for particular volumes may be calculated see Table 2

Table 2 Evaporation rates ml s^{-1} to drop volume.

V ml	t s	dV/dt ml s^{-1}
1.0	140.6	0.017
0.9	134.6	0.016
0.8	128.0	0.015
0.7	121.2	0.014
0.6	113.6	0.013
0.5	105.3	0.012
0.4	95.9	0.009
0.3	85.1	0.008
0.2	71.8	0.007
0.1	53.8	0.004

The values of evaporation rate (Table 2) to vapour flow rate (Table 1) are compared by display in Fig.4.

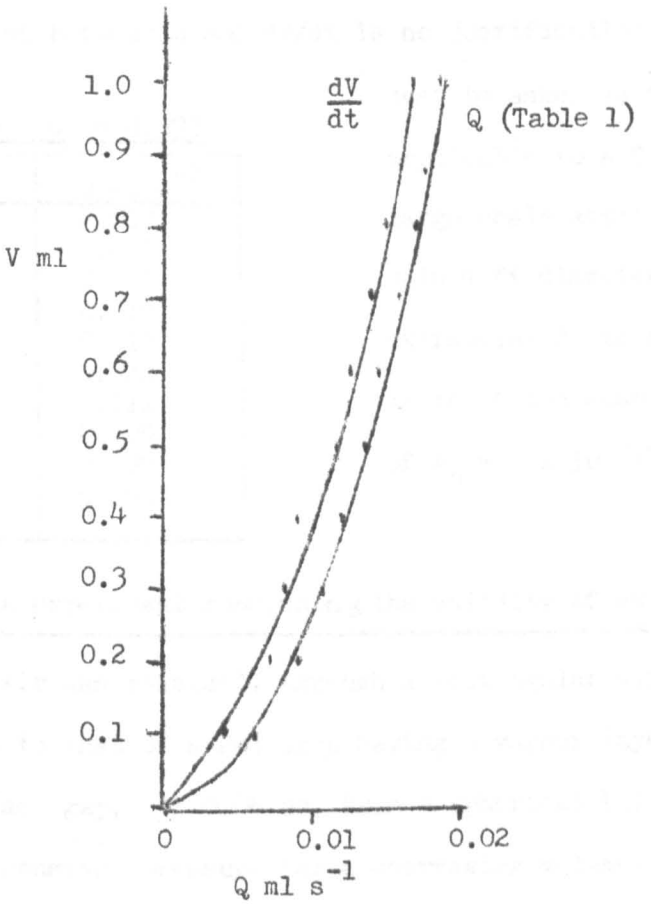


Fig.4 Drop volume (V) to Q and to dV/dt.

C_d values.

The immediate reaction to Fig.4 was that evaporation rate and 'escape' rate of vapour were demonstrated to be comparable. There is however the assumption that C_d values applicable in large scale hydraulic engineering - water mains, reservoir flow etc - are equally applicable to the small orifice beneath a Leidenfrost drop and the vapour flowing through the same.

No C_d value for water vapour has been located. If the lowest value for $C_d = 0.593$ (from Giles referred to earlier) is used then flow rates to drop volume are as in Table 3 which are in very close

agreement with dV/dt values, indeed for 7 out of the 10 volumes values are identical, However choosing a value of C_d which results in close agreement between Q and dV/dt is no justification for so doing. The question must be asked as to how far may conditions applicable to a C_d value determined from large scale applications (e.g. Water main 4 ft diameter, $A_o = 1.17\ m^2$) be extrapolated to an orifice, assumed to be of the same geometrical shape of $A_o = 3 \times 10^{-6} m^2$ (approx) ?

Table 3 $C_d = 0.593$

V ml	Q ml s^{-1}
1.0	0.017
0.9	0.016
0.8	0.015
0.7	0.014
0.6	0.013
0.5	0.012
0.4	0.011
0.3	0.009
0.2	0.007
0.1	0.005

A simple experiment concerning the validity of extrapolating C_d values.

Air was released, through a rectangular slit of similar area (1 mm²) and aspect ratio to that of a 2ml drop having a vapour layer thickness, drop to surface gap, of 0.06 mm, from a spherical balloon, to deliver air at constant pressure for a decreasing volume. Air pressure in the balloon was measured on a U tube manometer and balloon volume change was determined from change in diameter measured using outside calipers as air was released over 5 second intervals.

$$\text{Coefficient of discharge } C_d = \frac{Q}{A\left(\frac{2(p1 - p2)}{\rho}\right)^{\frac{1}{2}}}$$

$Q = m^3\ s^{-1}$

$A = m^2$

for $\rho = 1$ $C_d = 0.422$

$\rho = 1.3$ $C_d = 0.482$

$\rho = 1$ or $1.3\ kg\ m^{-3}$ (1.3 is the density given in Kaye & Laby, Tables of physical & chemical constants, 14 th ed. for atmosphere/air)

The values determined by this simple experiment indicate that the extrapolation of use of C_d values derived from large scale work is acceptable in investigation of vapour flow from the supporting vapour layer of a Leidenfrost drop. Values for Q for the Cd values obtained in the experiment are listed, with dV/dt values for comparison, in Table 4.

Table 4 Comparison of dV/dt with Q for C_d values obtained by experiment.

V ml	dV/dt	Q ml s^{-1} C_d = 0.482	Q ml s^{-1} C_d = 0.422
1.0	0.017	0.014	0.012
0.9	0.016	0.013	0.012
0.8	0.015	0.012	0.011
0.7	0.014	0.012	0.010
0.6	0.013	0.011	0.010
0.5	0.012	0.010	0.009
0.4	0.009	0.009	0.008
0.3	0.008	0.008	0.007
0.2	0.007	0.006	0.006
0.1	0.004	0.004	0.004

The comparison of Q to dV/dt indicates that the assumptions made were reasonable and that the vapour escapes at the evaporation rate indicating that the evaporation is maximum from the base of the drop into the supporting vapour layer from whence it flows through the drop/surface gap to atmosphere.

5.2.0. Concluding remarks and summary of results.

We now have a substantial amount of information on Leidenfrost drops; though a considerable amount remains for investigation of the subject as an aspect of boiling - which is not relevant here. From the studies of the Leidenfrost phenomenon undertaken for this investigation we are now in a position to determine the following information for a measured drop volume of initial concentration 3.5% Na Cl_{aq} for volumes $\leq$ 1 ml :-

Area of drop base exposed to heated surface A_b $= (190 \pm 4)$ V m^2

Vapour layer pressure $= 51.57$ Pa

Vapour layer thickness at drop edge $d = 0.06$ mm

Vapour flow rate Q from layer

$$= C_d A_o \sqrt{\frac{2(p1 - p2)}{\rho}} \quad \text{ml s}^{-1}$$

Area of orifice of escaping vapour $A_o = 2\pi r d$ (r to be determined from A_b, d = 0.06 mm)

Total evaporation time to drop volume

$$t = \left(\frac{V}{7.4 \times 10^{-9}} \right)^{\frac{1}{2.4}} \quad \text{s}$$

Drop volume V to total evaporation time t $V = 7.4 \times 10^{-9} \; t^{2.4}$ litres

Evaporation rate dV/dt $= 1.68 \; t^{1.4} \times 10^{-5}$ ml s^{-1}

The previously unsuspected phenomenon of a charging process emitting a charged particulate cloud from solution drops exhibiting the Leidenfrost phenomenon (4.3.3) discovered during this study will now be considered with respect to particle emission, particle size distribution and structure etc.

6.0.0 Particles from $Na\,Cl_{aq}$ solution drops, of initial concentration 3.5% (0.6 M), exhibiting the Leidenfrost phenomenon.

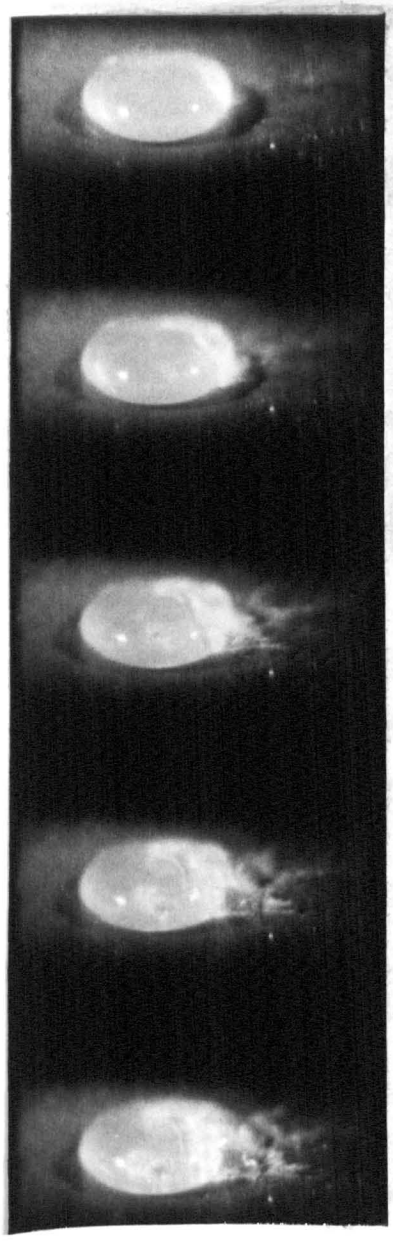
Introductory note.

Since some of the apparatus used to investigate particle emission and size was also used to study associated electrical activity it is sometimes neceasary in this chapter to refer to electrical features which will be considered in detail in chapter 7.

6.0.1 Observations of the emissions of particles.

The discovery of the emission of particles from a Leidenfrost drop, related in 4.3.3, was followed initially by naked eye observations of many such drops. From these it seemed that the particles might have their source in material which always seemed to be ejected laterally from the underside of the drop. To investigate this a Hitachi high frame speed camera was used to obtain a film record of particle emission as well as to observe drop behaviour during particle emission.

A drop was set up on a hot surface and when the first particle emission took place the camera was operated. Photograph 1 illustrates the condition of the drop at the onset of particle emission. The time between frames is 3×10^{-3}s. It will be observed that material is escaping from beneath the drop - to the bottom right of each picture. Photograph 2 shows the drop after a further 54×10^{-3} s have elapsed and the drop is obviously fragmented at one end and some of the larger droplets are visible. During the next 50×10^{-3} s approximately the drop reforms and glides quietly on the hot surface until the next particle emission occurs.



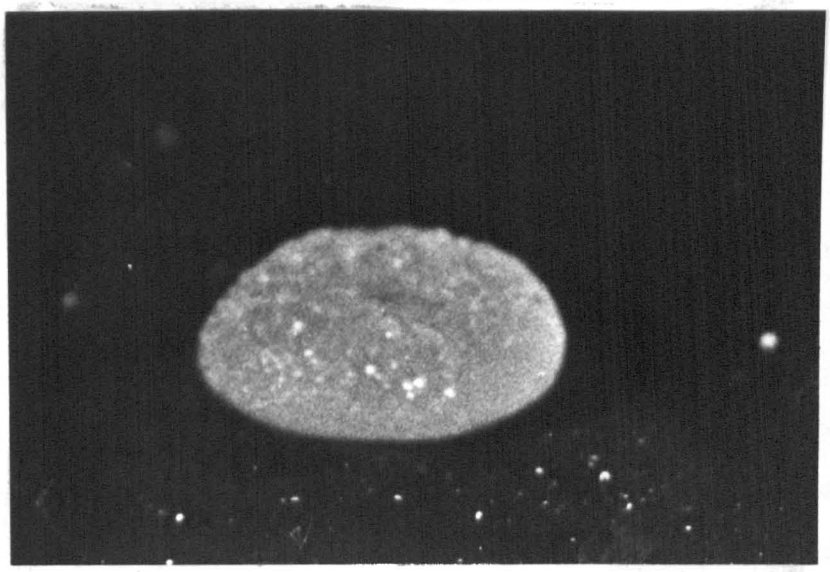
Photograph 1

Photograph 2

Particle emission - Hitachi high frame speed camera - 3×10^{-3}s between frames.

6.0.2 Particle emission related to solute precipitation.

As drops decrease in size, due to evaporation, small pieces of crystalline material may sometimes be seen inside them (The author first noticed this when sunlight shone on to a drop). On more rare occasions it appears as if the drop has been sprinkled with salt as in Photograph 3.



Photograph 3

A drop photographed when the surface was coated with crystalline salt.

Shortly after the appearance of the crystalline material the first emission of particles occurs.

The solubility of salt (Na Cl) is stated to be 35.7% at 0°C and 39.8% at 100°C (Kaye & Laby 1973 14th edition). Solution samples taken from drops at first particle emission for determination of concentration were examined in a Hilger and Watts Refractometer type M46 having a stated accuracy of 0.05%. It was found that particle emission seemed to occur at solute concentrations ranging from 26%to 30%. An explanation of the discrepancy between refractometer measurements and the stated concentrations for precipitation lies in the process of crystallization of Sodium Chloride from its aqueous solution. Kaufmann (1) has explained how evaporation from a Na Cl solution surface results in the concentration being higher there than in the bulk of the solution. The outcome of continued evaporation is the formation of crystals and, if the solution is still,these will grow and steadily sink to form hollow pyramids of solid Na Cl (so called Grainer salt). In the case of boiling solution vapour bubbles and

convection currents stir the crystalline material into the bulk solution. (This may be demonstrated by boiling $Na\ Cl_{aq}$ in a glass beaker illuminated from one side by light from a slide projector. Crystalline material (salt) will be visible as glistening fragments - a refractometer measurement of concentration when these were first seen was 26%).

In a Leidenfrost drop maximum evaporation is taking place near to the hot surface and solution concentration will therefore be highest on the underside surface. A sample extracted for the refractometer is most unlikely to be from the precipitating surface only and will be diluted by bulk solution. Both drop motion and internal convection will contribute to this. The conclusion must be made that the usual method of the determination of solution concentration viz. by use of a refractometer is not reliable with Leidenfrost drops. For the purposes of this investigation the precipitation of $Na\ Cl_s$ will be expected when the concentration of the solution reaches 39.8% (Kaye & Laby).

6.0.3 The crystalline skin and particle emission mechanism.

The extensive work of Kaufmann (ref 1) has indicated that a crystalline layer will form on the surface of a saturated solution of Na Cl left exposed to the air. The author confirmed this i.e. Kaufmann's claim, by leaving several litres of saturated $Na\ Cl_{aq}$ exposed to the air. A thin crystalline layer was formed on the surface of the solution, in parallel sided glass jars 18 cm diameter, and crystals grew on the solution side of the layer giving it an irregular thickness. Sections of the layer broke away and sank into the solution. It was also found that a small red hot filament supported above and nearly touching the surface of the solution would produce a crystalline layer or skin immediately below the filament. A drop of solution placed on a greased microscope slide, to form a drop, with a small filament mounted above it permits the formation of this crystalline skin to be observed under a microscope. (Set up as in Fig.1).

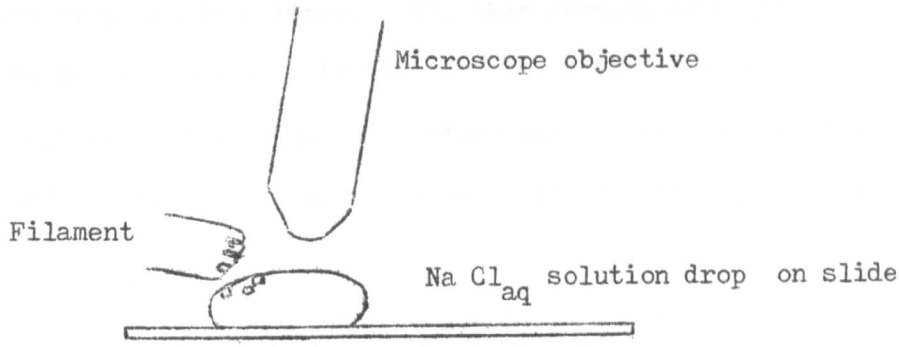


Fig.1 An arrangement for observing the formation of the crystalline skin due to evaporation.

Tiny groups of cubic crystals join to form patches of crystalline skin. Some of these grow faster than others but in a haphazard manner until the entire surface is covered. This growth and development of the skin is illustrated in Fig.2.

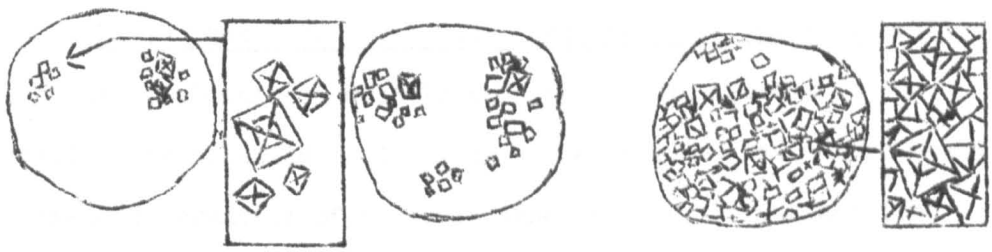


Fig.2 The growth and development of a crystalline skin.

Examination of this skin shows that its haphazard superficial growth is accompanied by a similar haphazard tendency to develop into the solution as shown in the cross section of a sample of the skin in Fig.3.

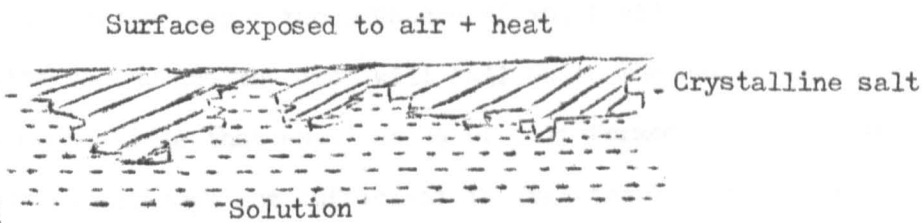


Fig.3 A cross - section of crystalline skin.

Continuous application of heat to an area of the crystalline skin produces small bubbles of vapour which, on bursting, rupture the relatively smooth surface. The skin forming on solution subjected to vibration (for example by placing the slide into the cone of a loudspeaker fed from an oscillator) will often have jointed blades of solid salt instead of the more familiar cubic crystal structure - Fig.4.

Fig.4 Sketch of crystalline skin produced during vibration.

If a Leidenfrost drop is considered with respect to the precipitation of solid Na Cl it is to be expected that there would be a haphazard formation of a crystalline skin on the surface from which maximum evaporation was taking place. The haphazard formation is probably due to two factors (i) the presence of nuclei, which in Leidenfrost drops are likely to be oxide fragments swept up from the hot surface, for the formation of crystals, (ii) the motion of the liquid by convection currents and drop movements. As precipitation continues the underside of the drop will in due course be covered with a crystalline layer, the presence of which will shut off the supporting vapour and the drop will fall on to the heated surface. It is also possible that small areas of salt formed on the underside of the drop, although not sufficient in area to cause the support system to fail, may be disrupted by the bursting of bubbles which cause part of the crystalline material to project below the drop and touch the hot surface.

Consider the section of the drop touching the hot surface. Bearing in mind that the solution exists as a Leidenfrost drop due to evaporation it is unlikely that solution boiling alone is the cause of the 'explosive' particle emission with its attendant audible,"Crack!"

A phenomenon known as decrepitation occurs when certain salts are heated. A search of chemical literature reveals that there is virtually no information on this phenomenon other than to define it. A definition generalised from three sources combined [2,3,4] is that decrepitation is, 'Physical rending or flying apart of the joints of the crystalline structure of certain minerals and salts due to internal stresses when heated. It is attended with a crackling noise'. Several chemists [5,6,7] suggested that water of crystallization would provide an explanation but others suggested internal stresses or entrapped liquids.

In a series of qualitative experiments in which (i) various crystals were heated on a metal plate, (ii) were heated and cold solution dripped on to them,(iii) were heated and dropped into cold solution: it was found that crystals having water of crystallization produced little or no decrepitation but those without would fragment violently and noisily. Characteristics appertaining to Na Cl are :-

(i) Crystals placed on a hot surface explode into fragments.

(ii) Crystalline flakes precipitated from a boiling solution and still wet fragment violently on a hot surface.

(iii) Crystalline flakes dried slowly fragment in less quantity on a hot surface.

(iv) Slowly dried flakes placed on a hot surface and water dripped on to them will fragment in greater quantities than when left in a dried condition.

(v) Heated crystals dropped into cold water fragment but with little violence.

(vi) Fragments of crystals possess an electric charge.

Crystalline material precipitating from a solution will not only be wet but will most likely contain occluded brine (see Kaufmann[1]). The pressure of such occluded brine varies with temperature :-

$$\frac{dp}{dT} \approx -\left[\frac{\alpha(\text{brine}) - \alpha(NaCl_{(s)})}{\beta(\text{brine}) + \beta(NaCl_{(s)})}\right] \text{ Pa } {}^{\circ}C^{-1}$$

where, α (brine) is the volume thermal expansivity of brine
" $\alpha(NaCl_{(s)})$ " " " " " of solid sodium chloride
" β (brine) " " isothermal compressibility of brine
" $\beta(NaCl_{(s)})$ " " " " of solid sodium chloride

Take α (brine) $\simeq \alpha$ (water) $= 22.5 \times 10^{-5}\ {}^{\circ}C^{-1}$ at 100°C } Handbook of Chemistry & Physics Chem. Rubber Co. 54th edn
β (brine) $\simeq \beta$ (water) $= -48.9 \times 10^{-11}\ Pa^{-1}$ at 100°C }
$\alpha(NaCl_{(s)}) = 4.0 \times 10^{-5}\ {}^{\circ}C^{-1}$ at 100°C } Kaufmann (1)
$\beta(NaCl_{(s)}) = -4.5 \times 10^{-11}\ Pa^{-1}$ at 100°C }

$$\therefore \frac{dp}{dT} \approx 3.5 \times 10^{5}\ Pa\ {}^{\circ}C^{-1}$$

A crystal forming on the underside of a Leidenfrost drop will be at a temperature of about 100°C. When this crystal contacts the hot surface which is at a temperature of about 600°C the $NaCl_{(s)}$ and the brine will begin to rise in temperature at a rate determined by the thickness of Na Cl_s between it and the hot surface and also on the thermal conductivity of Na Cl. (Thermal conductivity of Na Cl_s ranges from 0.01 W s^{-1} m^{-1} $^{\circ}K^{-1}$ at 100°C to 0.00497 at 400°C for single crystals, 0.0228 for Na Cl from solution at 0°C). For each 1°C rise in temperature the excess pressure increase of the occluded brine is about 4×10^5 Pa. Depending on the strength of the confining walls this pressure will continue to increase with temperature until the crystal violently fragments, that is decrepitates.

A crystal contacting the hot surface will also begin to expand (The linear coefficient of expansion = 3.9×10^{-5} approx, cubical coefficient = 1.2×10^{-4}). Although Na Cl is plastic it is only so under a steady force applied over a long period of time amounting to several days (Kaufmann ref 1). Thus the crystal will be expanding more rapidly on its lower side and imposing strain on the material above it.

The low plasticity or brittleness of Na Cl_s will cause the crystal to break up, that is to decrepitate.

Any solution in cracks in the crystal surfaces will exert pressure due to heating and, depending on the strength of the walls around it will ultimately break the crystal.

Decrepitation is a field for investigation in its own right but results from the few experiments with Na Cl and other materials leads to a reasonably confident proposal that when a Leidenfrost drop forms a crystalline skin on its underside which causes the vapour support to fail then the drop will fall on to the hot surface and crystalline decrepitation for one or all three reasons just outlined will cause the 'explosion' of Na Cl_s and it is this material escaping along the metal - hot - surface which causes particle emission (see Fig 5). The particles, it would seem, will evolve from this solid material and saturated solution torn from the underside of the drop (see also Photographs 1 and 2) and flung clear of the drop by crystalline decrepitation. The mechanism would be expected to operate at the

Crystalline Skin Forming

Contact with hot surface and decrepitation with particle emission.

Fig.5

Details of particle emission mechanism due to shutting off of vapour support system by formation of crystalline layer on underside of drop.

base of the drop since it is there where maximum evaporation will be taking place due to the heated surface and such evaporation will produce a more saturated solution from which there will be precipitation of solid material leading to particle emission. The mechanism will be haphazard in initiation due to the formation of the skin and the decrepitation of the crystalline salt in this skin when it touches the surface. In addition to this, the behaviour of the saturated

solution (i.e. whether it remains in the region of the lower surface or is stirred by drop motion) is also a haphazard feature.

A simple demonstration of the emission of particles from below a drop may be made by heating a wire gauze red hot and carefully setting up a solution drop. On particle emission, material may be observed being 'fired' through the holes in the gauze as emission takes place from the underside of the drop.

Predicting particle emission with respect to drop volume and time.

Despite the haphazard behaviour of the precipitation forming a skin and the onset of particle emission some possibility exists to predict at what volume and after what period of time the first particle emission may be expected to occur.

Precipitation can be expected to occur when solution concentration is 39.8%. In terms of drop volume this would involve a reduction factor (f_r)

where $f_r = \frac{A_2 \text{ (the concentration at precipitation)}}{A_1 \text{ (the initial concentration)}}$ ---(1)

If V_1 is initial drop volume and V_2 is the volume of the drop at first particle emission then :-

$$V_2 = \frac{V_1}{f_r} \text{ ----------(2)}$$

$$= \frac{V_1 A_1}{A_2} \text{ ----------(3)}$$

(3) enables us , if we know the initial drop volume and solution concentration, to predict that particle emission should occur when the drop has reached the volume V_2. This equation relates particle emission to concentration of solute and drop volume.

Knowing V_2 it is possible to find the time from drop initiation to first particle emission from the evaporation graph (Fig. 1 & 2, 5.1.1)

However if we let t_p = time to first particle emission

t_{V_1} = total evaporation time of drop of initial volume V_1

t_{V_2} = total evaporation time of drop of initial volume V_2

then $$t_p = t_{V_1} - t_{V_2} \quad \text{---------(4)}$$

from (6) of (5.1.1)

$$t_{V_1} = \left(\frac{V_1}{7.4 \times 10^{-9}} \right)^{\frac{1}{2.4}} \text{ s} \quad (V \text{ in litres})$$

$$t_{V_2} = \left(\frac{V_2}{7.4 \times 10^{-9}} \right)^{\frac{1}{2.4}} \text{ s} \quad (V \text{ in litres})$$

from (3) $$t_{V_2} = \left(\frac{V_1 A_1}{7.4 \times 10^{-9} A_2} \right)^{\frac{1}{2.4}} \text{ s}$$

therefore $$t_p = \left(\frac{V_1}{7.4 \times 10^{-9}} \right)^{\frac{1}{2.4}} - \left(\frac{V_1 A_1}{7.4 \times 10^{-9} A_2} \right)^{\frac{1}{2.4}} \text{ s} \quad \text{----(5)}$$

where V is in litres and A in % or Moles.

(5) may be simplified to :-

$$t_p = (1.35 \times 10^8 V_1)^{\frac{1}{2.4}} - ((1.35 \times 10^8 V_1 A_1) A_2^{-1})^{\frac{1}{2.4}} \text{ s} \quad \text{--(6)}$$

According to (6) a 1 ml drop of initial concentration 3.5% $Na\,Cl_{aq}$ t_p = 87.44 seconds. Experimentally determined times from 10 such drops gave a time to first particle emission = 70 ± 2 s.

Remembering that the emission mechanism is haphazard in behaviour, equation (6) is very useful. The too high value will be in part due to the haphazard mechanism and also possibly to the fact that only the

lower surface of the drop needs to be at 39.8% concentration for precipitation and first particle emission to occur - i.e. the whole solution need not be at 39.8% for first particle emission.

For practical purposes a correction factor of about 0.8 applied as a multiplier to equation (6) gives first particle emission time values near to those found in experiments, that is, experienced in practice:-

$$t_p = 0.8\left((1.35 \times 10^8 V_1)^{\frac{1}{2.4}} - (1.35 \times 10^8 V_1 A_1) A_2^{-1})^{\frac{1}{2.4}}\right) s \quad ---(7)$$

6.0.4 The number of particle emissions from 1 ml drops of 3.5% $Na\,Cl_{aq}$

A probe inserted into a drop and connected to an electrometer had shown that each particle emission was accompanied by a pulse of electricity. The apparatus sketched in Fig.6 was used to count these pulses and thereby the number of particle emissions from 1 ml drops.

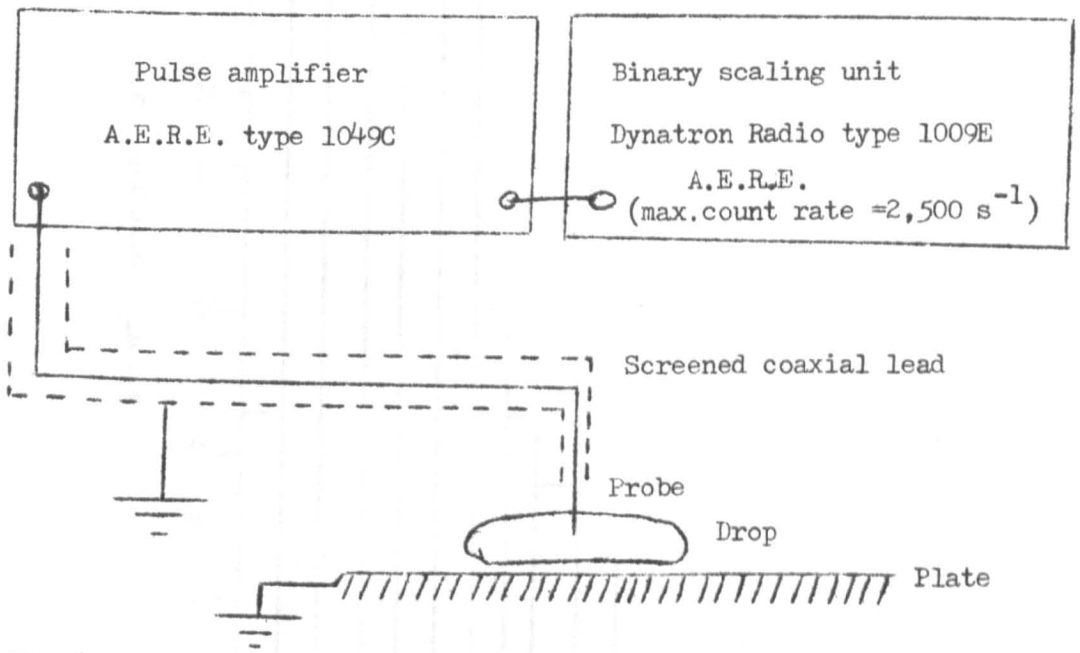


Fig.6 Apparatus for counting pulses from Leidenfrost drops during particle emissions.

The counts recorded by this apparatus are displayed in Fig.7. There are not the same number of particle emissions from each drop - the least count = 613 and the most = 2,777, the average = 1,444.

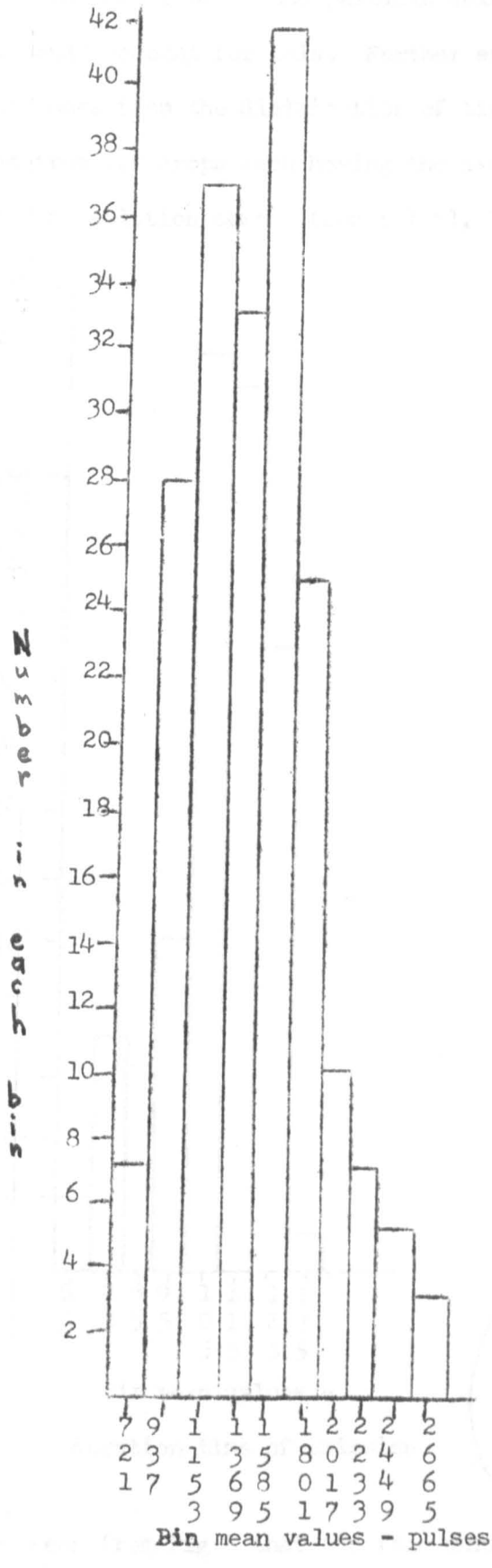


Fig 7 Count of

Pulses from 1 ml drops.

(Each bin = 216

Bin subdivision e.g.

Bin 1 from 613 up
to and excluding 830.)

The haphazard behaviour of the particle emission mechanism, discussed earlier, would account for this. Further evidence of this haphazard behaviour comes from the distribution of time for total emission of particles from 100 drops each having the same initial parameters of volume and solution composition (1 ml, 3.5% Na Cl_{aq}) (Fig. 8)

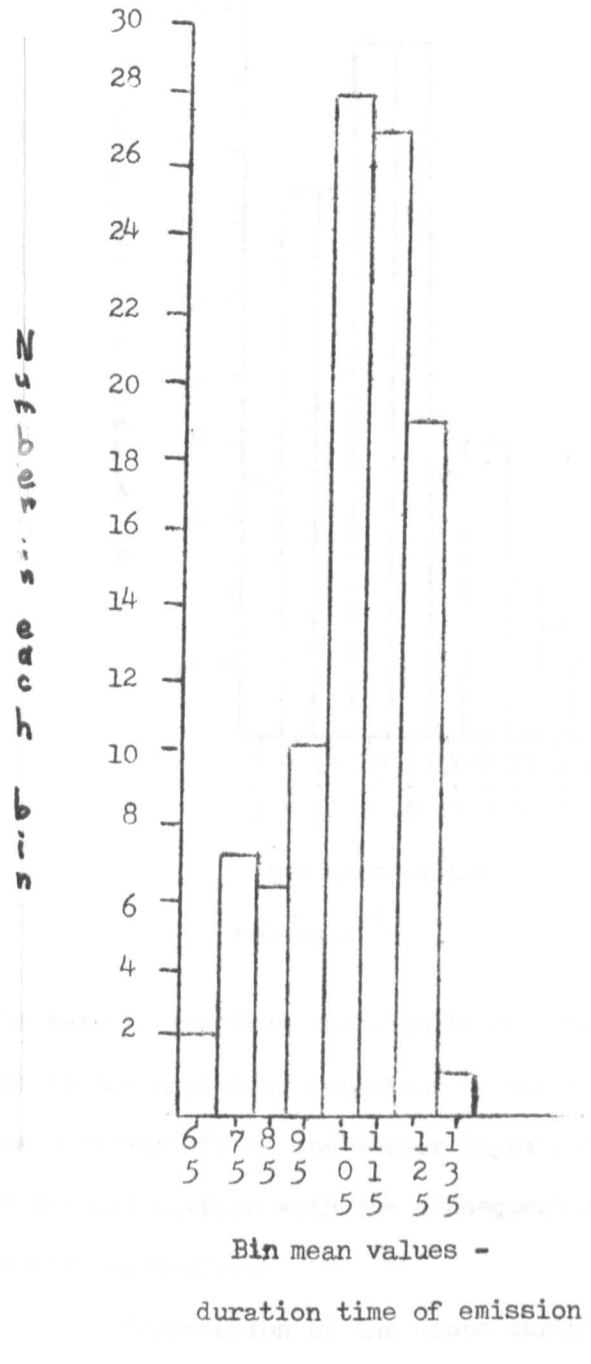


Fig.8 Duration of total particle emission of a 1 ml drop.

(Each bin = 10 s
Bin subdivision e.g.
Bin 1 from 60s up to
and excluding 70 s)

It will be seen from Fig 8 that the time during which particles are being emitted is not the same for each drop.

The rate of particle emission from each of the 100 drops:-

$$\frac{\text{Number of pulses counted (particle emissions) per drop}}{\text{Duration of particle emission per drop}}$$

is displayed in Fig.9

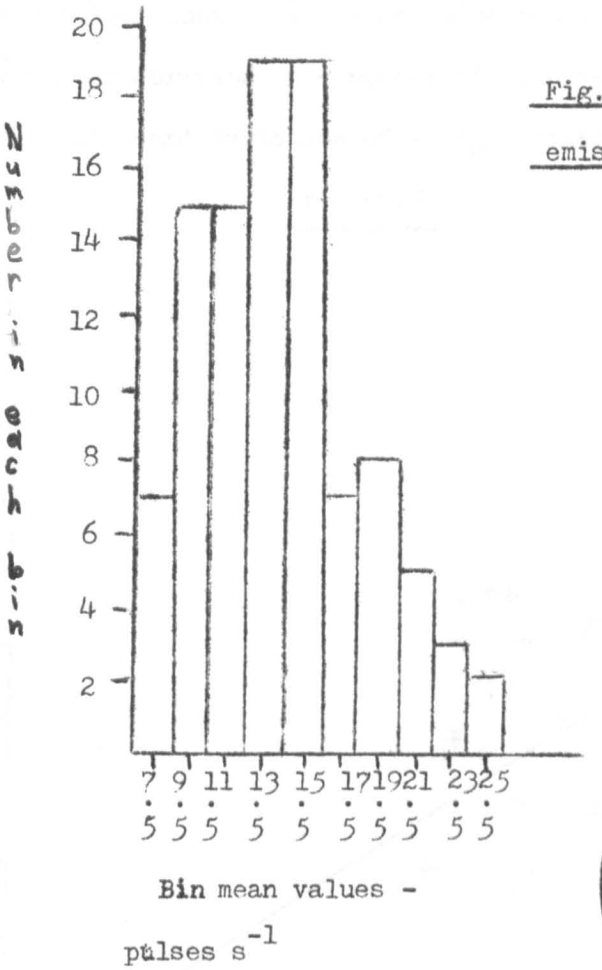


Fig.9 Rate of particle emission from a 1 ml drop

The rate of particle emission is not the same for each drop, again due to the haphazard behaviour of the forming of the crystalline skin, the shutting off of the vapour layer and the falling of the drop on to the hot surface with the consequent emission of solution droplets to form particles.

Observation of the drops during the counting of pulses (from which Fig.7 was obtained) gave the feeling that a greater number of counts was produced during a longer duration time. To test for a correlation between the number of emission counts and the duration times

for the total number of particle emissions from individual drops the two were plotted and an attempt made to fit a straight line (Fig.10)

Coefficient of correlation $r = \dfrac{\frac{1}{n} \sum (x - \bar{x})(y - \bar{y})}{s_x s_y}$

where x = pulse count $\bar{x}$ = mean pulse count y = duration

$\bar{y}$ = mean duration n = number of observations

s_x = standard deviation of x s_y = standard deviation of y

$r = +0.3$

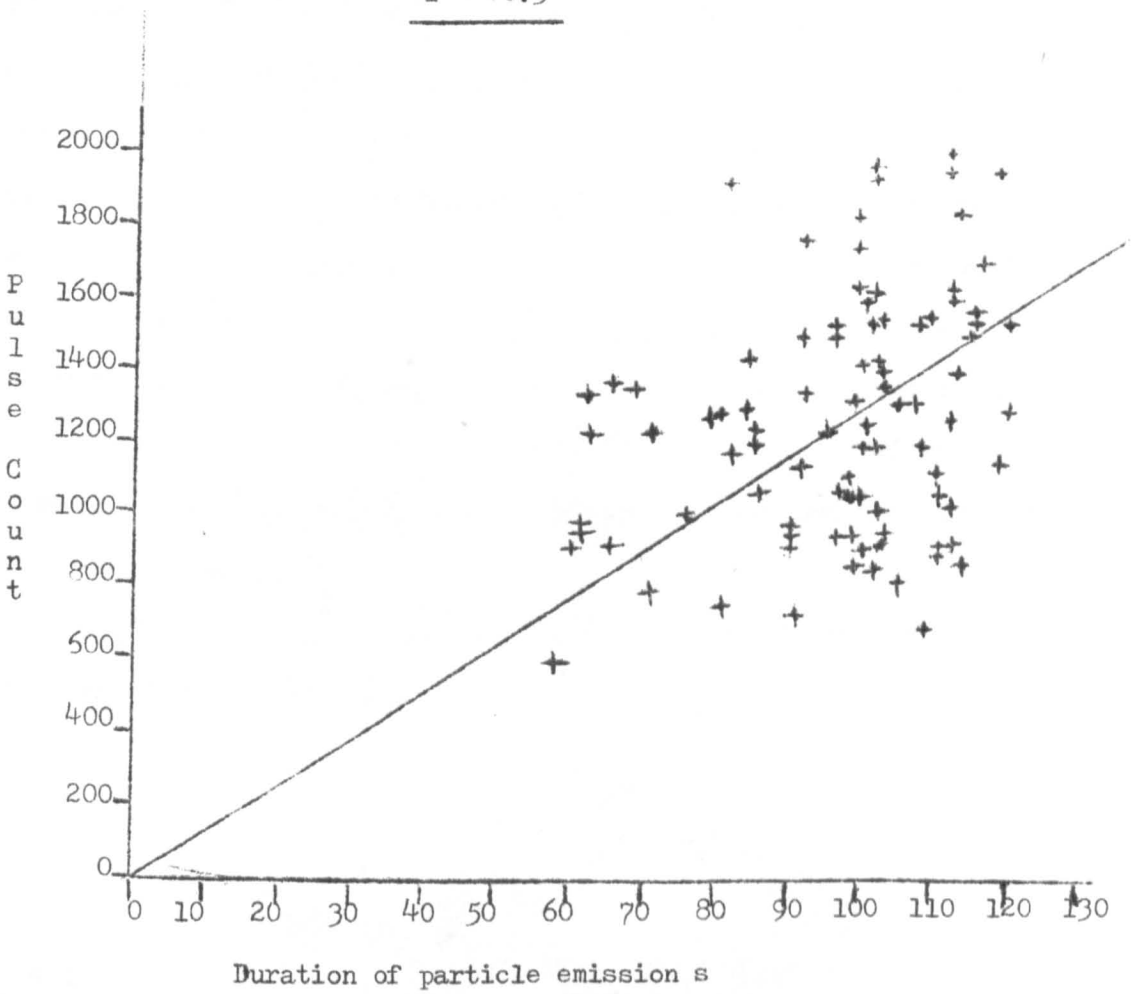


Fig. 10 Pulse count to duration of particle emission. Particle emission rate.

Thus a weak correlation is indicated between the number of particle emissions from an individual drop with respect to duration time of total number of emissions from that drop. Continued observations

confirmed that a drop which is emitting particles over a longer duration would not necessarily produce more or as many particle emissions as a drop emitting particles over a shorter duration. From which it appears that no relationship exists between particle emission count and the duration of these emissions since a haphazard mechanism is in operation.

6.0.5 The number of particles produced in each emission.

Although it is impossible to predict the direction in which particles will be emitted from beneath the drop an attempt was made to count how many particles i.e. solution droplets giving rise to particles, are produced on each emission. Mason [8] has described two methods by means of which droplets may be recorded on prepared glass slides. An oxide coating from burning magnesium ribbon may be deposited on a clean slide or , alternatively, soot may be used for the same purpose. Droplets reaching a prepared slide will be recorded as discs in the coating. Trials showed that a soot layer was the best medium in this case since difficulties were experienced in forming an even layer of M_g O and the salt precipitated from droplets made some discs difficult to see.

A prepared slide was held, in forceps, with its face parallel to the edge of a drop as shown in Fig. 11

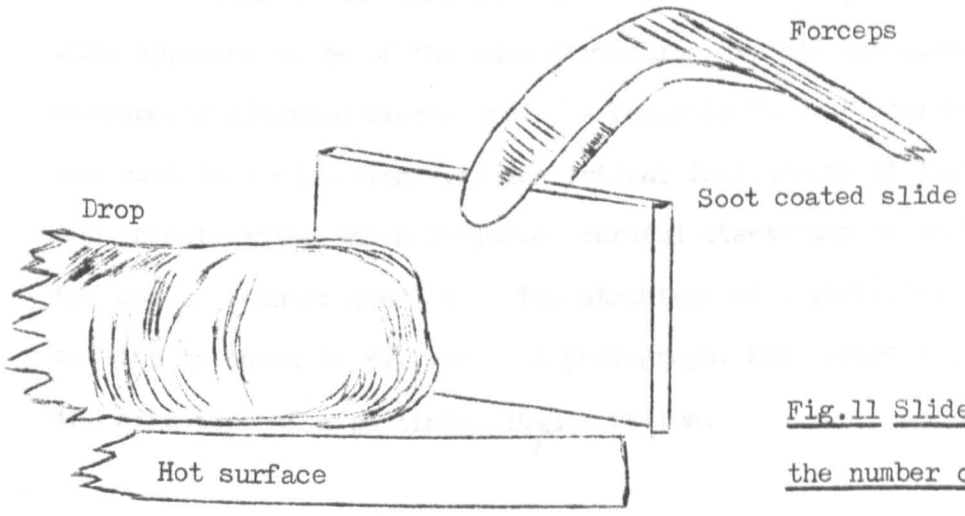


Fig.11 Slide to record the number of droplets produced by a particle emission.

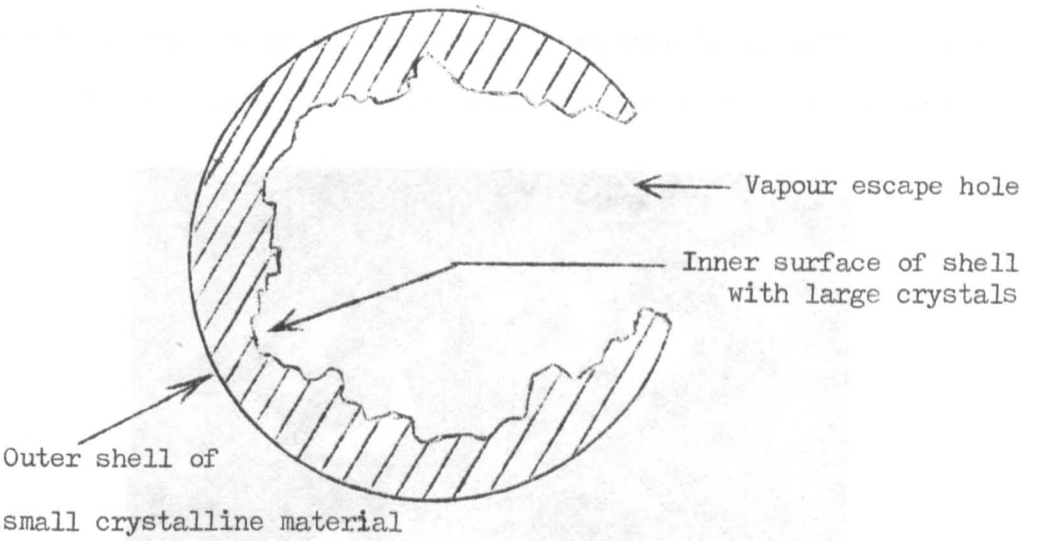
When a particle emission was heard the slide was remaoved and held in front of a lamp for examination. Only one particle emission was caught on each slide. A count was made of the discs on each slide by placing it under a microscope and using transmitted light. The assumption was made, on the basis of all discs being close together, that all droplets, recorded as discs, emitted in an emission were caught.

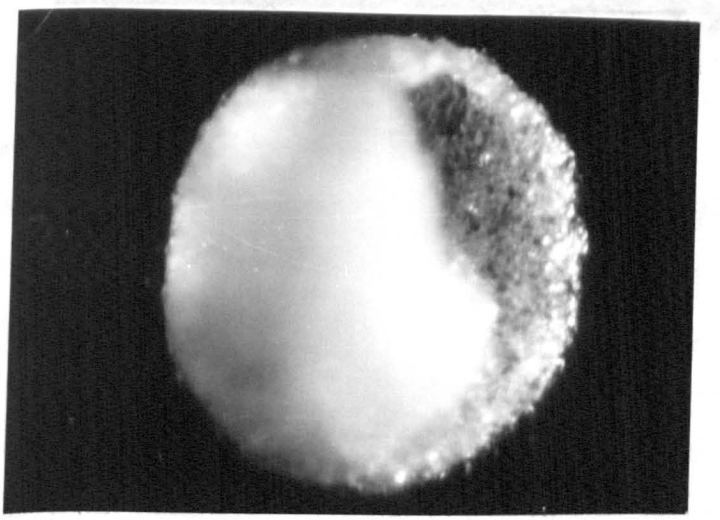
Drops do not produce the same number of droplets, which are the progenitors of particles, the maximum counted = 708, minimum = 198 and the average = 450. Since the average number of particle emissions from one drop is approximately 1,500 and the average number of particles produced during each emission is 450 then a Leidenfrost drop of initial volume 1 ml (10^{-3} litres) having an initial Na Cl concentration of 3.5% produces, on average, 1,500 x 450 = $\underline{6 \times 10^5 \text{ particles.}}$

6.0.6 Particle structure.

Particles were collected for examination by carefully moving a transparent polystyrene bar , (Rectangular cross-section 1.25 cm x 0.5 cm x 10 cm) charged by rubbing, above and around a drop which was emitting particles. The captured particles were examined under optical microscopes (Reichert or a Watson Stereoscopic or a Russian Biolam 14) and were found to all have the same structure. Samples of the smallest also appeared to be of the same structure and this was confirmed by a Stereoscan electron microscope. A Polaroid ED - 10 microscope camera was used in conjunction with the optical instruments at this stage of the investigation which included careful dissection of particles by the use of mounted needles. The structure of a particle, in cross-section is shown in Fig. 12. A photograph, Photograph 4 illustrates the structure of a particle 10 μm radius.

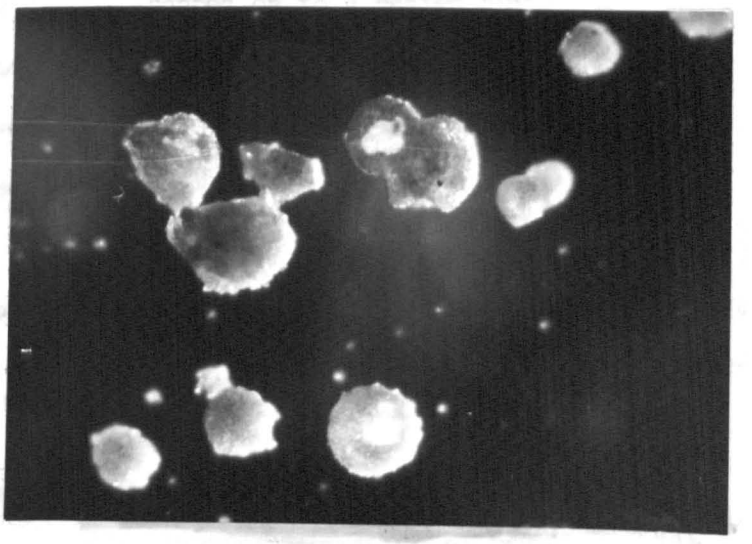
Fig.12 Cross - section of a salt particle.





Photograph 4. A salt particle. (The inside of the particle walls are visible revealing a coarse crystalline structure. The thickness of the wall may be observed and of course the spherical shape of the particle.)

Several particles are shown in Photograph 5 taken in part reflected, part transmitted light to give some indication not only of structure but of the thinness of the particle walls - which shows as brighter areas in the particle bottom centre and almost immediately above top picture where light is passing through the walls and shining out through the hole in the particles. Spherical structure is apparent. Several, out of focus, smaller particles appear in the general background.



Photograph 5 Salt particles from a Leidenfrost drop.

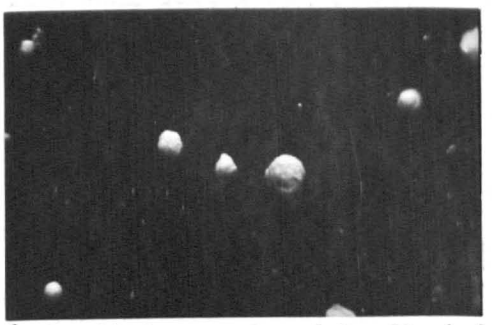
Photographs 4 & 5 were obtained using a Minolta SRT 303 camera fitted with a microscope adaptor to a Russian Biolam 14 microscope. Ilford FP4 125 ASA, 35 mm film was used.

All particles have an outer crystalline shell in which no regular i.e. cubic, crystal structure is obvious, which suggests rapid formation from solution, and a coarser inner lining to this shell often with cubic crystals, indicating less rapid formation. The particles bear a strong similarity of appearance to quartz geodes familiar to geologists and of late to Lapidary dealers. Each particle has one or more roughly circular holes, though most have one hole, as if material has escaped from the inside of a once closed sphere.

Particles from flash boiling.

The author stated, in the critique ending chapter 3, that although a particle was mentioned, by Woodcock et al, no such particle was described. During the investigation of particle structure it was considered useful if a diversion was made to examine the particles supposed to be produced by flash boiling of Na Cl_{aq} (see 4.1.0 for definitions of forms of boiling).

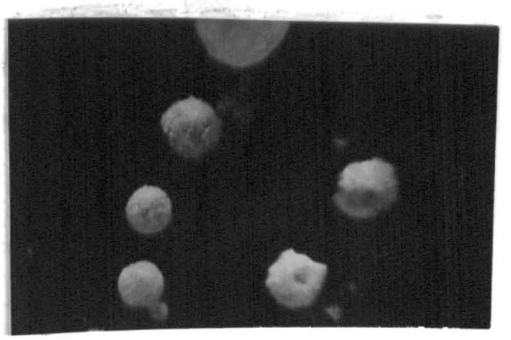
Solution was dropped on to a heated surface, spread out, and evaporated in a few seconds. Charged polystyrene rods were passed to and fro above the flash boiling solution. Examination of the rods under the microscope revealed many tiny spherical particles which on further examination were found to be of the same structure as those produced by Leidenfrost boiling. Photograph 6 illustrates some of these particles. They were produced in much greater numbers and were noticeably smaller in size.



Photograph 6. Particles produced by flash boiling 3.5% Na Cl_{aq}.

Particles from an aerosol spray gun.

A hand operated spray gun was filled with saturated Na Cl_{aq} solution and the spray produced from this was directed over and above a large copper dish heated to red heat, by gas jets. A charged rod was used to collect many particles which, on examination, were found to have the same structure as those from Leidenfrost and flash boiling - see Photograph 7



Photograph 7. Particles produced by a spray gun.

The structure of these particles, indeed the confirmation of their very existance, had not previously been published and details were published by the author (Pounder 1975 [9]).. Blanchard[10] confirmed that neither he or his co-workers had ever seen the spherical shaped particles and that Woodcock and Spencers' publication did not offer any conclusive evidence for their existance. Apparently the particles/nuclei seen in investigations of bursting bubbles are, 'misshapen globs of salt' or small cubic crystals.

It does seem from this investigation that spherical crystalline particles are the rule rather than the exception when produced from evaporating solution droplets. Blanchard [10] wondered if this was perhaps the case only with hot solutions - used by the author -but a saturated drop held on a glass support produced the outer shell of a 'particle', before being blown away, when held in a cold air stream from a hairdryer. (The formation of particles will be dealt with in the next section.) It is known that spherical particles are produced in dryers in the Chemical Industry [11] but this is the first time that they have been described for flash boiling and certainly for particles emitted from solution undergoing Leidenfrost boiling.

The similarity in structure of particles produced from various forms of boiling would present difficulties in identification of their source by impactor sampling. It would seem necessary, in the field, to identify the forms of boiling taking place by direct observation of lava entering the sea. In the case of aqueous solutions in crater lakes

this may be an impossible task.

6.0.7 Particle formation.

The structure of particles and the mode of their emission, see Fig.5, led the author to consider the following hypothesis as to their formation. Each particle is emitted from the parent solution drop as a tiny droplet of saturated solution. As it moves through the air water will evaporate from its surface and the solution will become most concentrated there and precipitation of salt will take place. The precipitation, haphazard in behaviour due to the unpredictable location and presence of the necessary nuclei for crystal formation, will in due course cause the outer surface of a droplet to be covered with a solid layer or shell. Crystallization will continue on the inside of this shell at a slower rate and (i) either steam or (ii) remaining solution will break out through the weakest part of the shell. The result would be a hollow spherical particle with a wall of irregular thickness, due to internal crystallization, and a vapour or solution escape hole.

To test the hypothesis under controlled conditions, the following procedure was used. Pieces of glass rod were heated and then quickly drawn out to give very fine needles of glass. On to such a needle a droplet of saturated $Na\,Cl_{aq}$ solution was carefully placed, by dipping the needle into a beaker of solution, withdrawing it and carefully tilting the needle to form a droplet as shown in Fig. 13

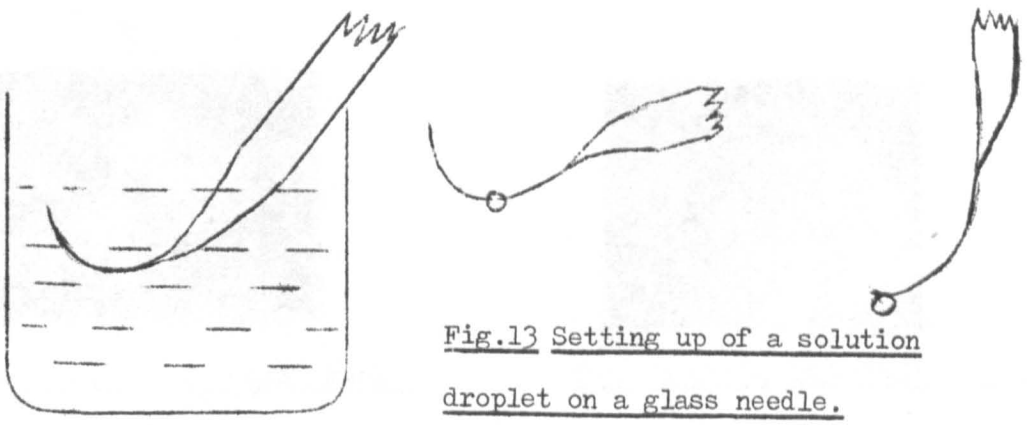


Fig.13 Setting up of a solution droplet on a glass needle.

The needle and droplet were set up under a microscope. A coiled filament was brought near to the droplet and the heat of the filament, controlled with a rheostat, could be varied thereby controlling the evaporation from the droplet - see Fig.14

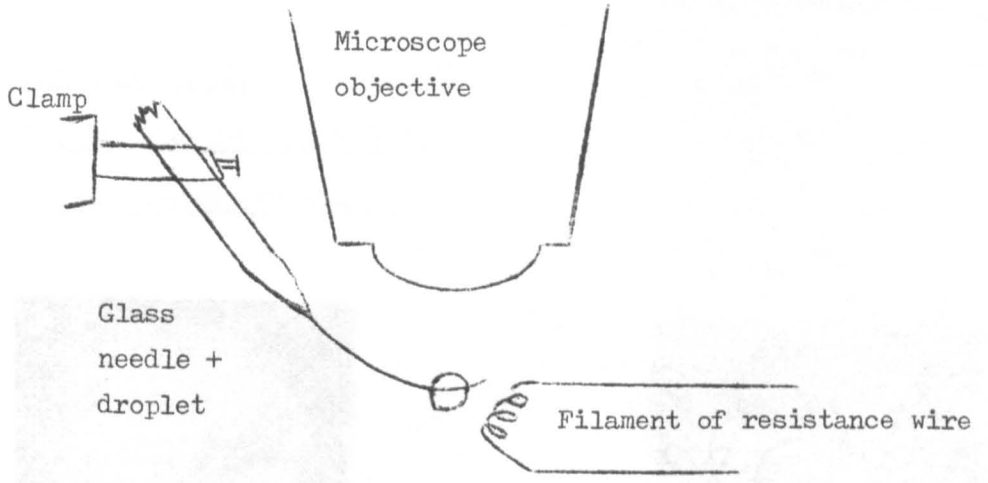
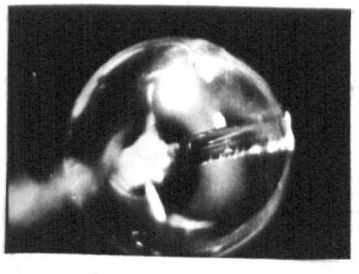
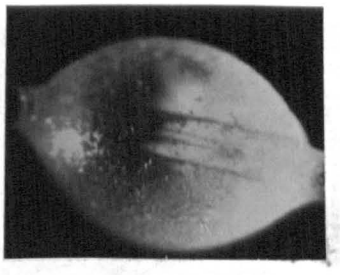


Fig.14 Apparatus to investigate the formation of a particle from a droplet of Na Cl_{aq} solution.

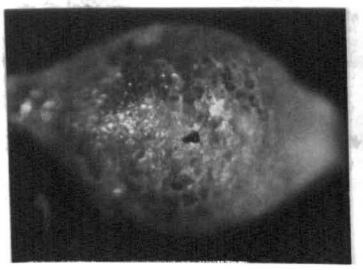
The sequence of photographs 8 to 12 show how a droplet, about 2 mm diameter, becomes gradually covered with a crystalline skin. Shortly after the whole surface has been covered a faint audible, "Pop!" was heard and the surface was ruptured by escaping vapour which left the familiar hole observed in a particle. In this case the hole (Photograph 12) had a shape somewhat like that of a trumpet bell which indicated that it had been formed by solution or vapour escaping from the inside of the crystal shell.



Photograph 8. Solution droplet on glass needle.

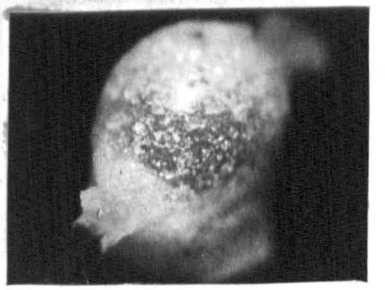


Photograph 9. Crystalline shell forming, needle still visible through uncovered solution.



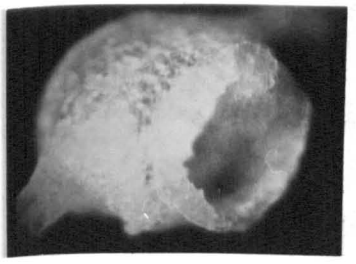
Photograph 10.

Crystalline shell completely covering entrapped solution



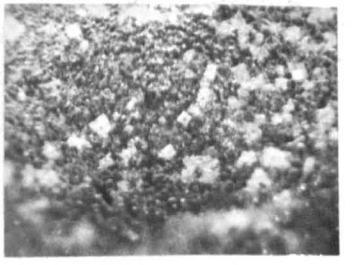
Photograph 11

Crystalline shell of dry particle - opposite vapour escape hole



Photograph 12

Vapour/solution escape hole



Photograph 13

Inside surface of particle showing some cubic crystals

It would seem reasonable to claim that the hypothesis proposed to explain particle formation is acceptable. No attempts to make measurements of any kind were undertaken the aim being simply to test the hypothesis of particle formation. One feature which could have two possible causes is that of the hole in each particle.

(i) The water component of the solution trapped within the shell may turn to vapour and in undergoing the phase change seek to take up a larger volume and so exert a pressure which breaks through a weak section of the shell wall. (The experiments from which the above photographs were taken demonstrated this.) This might be the case of particles travelling in the vicinity of the heated surface or in convection currents rising therefrom.

(ii) Once the crystalline shell has formed and trapped solution within it slower crystallization will continue on the inside walls and the formation of cubic crystal structure, requiring as it does greater volume, will exert pressure on the remaining solution and so again the weakest section of the wall gives way. It should be noted that in this case the precipitation need not be due to evaporation but to the cooling of the entrapped solution. Solubility curves for Na Cl show that salt is precipitated at a rate of about 1% per 20°C or 0.05% $^{\circ}C^{-1}$ fall in temperature of the solution.

6.0.8 Particle size.

Particles were caught on charged polystyrene rods, as described earlier, and the diameter of individual particles was measured by means of a micrometer eyepiece. The size distribution measured by this method is shown in Fig. 15. The larger particles, those ranging in size from about 50 μm upwards, are usually to be found on the heated surface where they have been observed to form from droplets which, after leaving the drop, roll on the hot surface.

The Dark Field Ultramicroscope.

In order to measure the electrical charge on individual particles, an offshoot of which is also to measure their radius, a version of the dark field ultramicroscope described by Kunkel and Hansen [12] was constructed. A cross - section of the layout of the instrument is shown in Fig.16. The principle of the instrument is based on the forward scatter of light, into the camera, from anything passing through the focal point of a cone of light having a dark cone within it. This point is set up to be between two parallel conducting surfaced glass slides (G). To set up the instrument a hair weighted with a lead shot is carefully positioned so as to hang through the focal point. The camera may now be focussed sharply on the hair. A graticule calibrated in mm squares is next located in the same position and photographed for later measurements of the tracks of particles recorded on negatives.

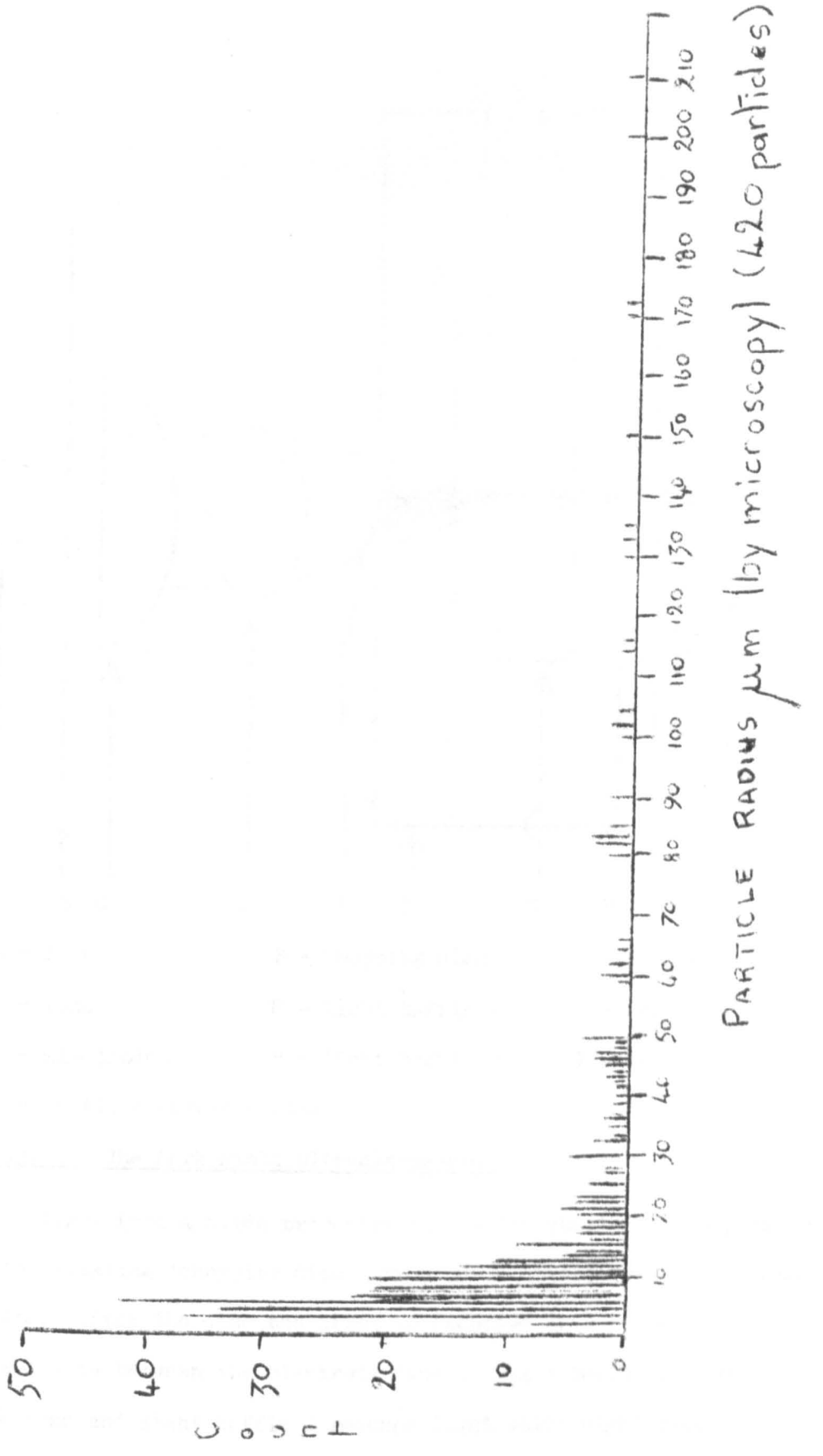
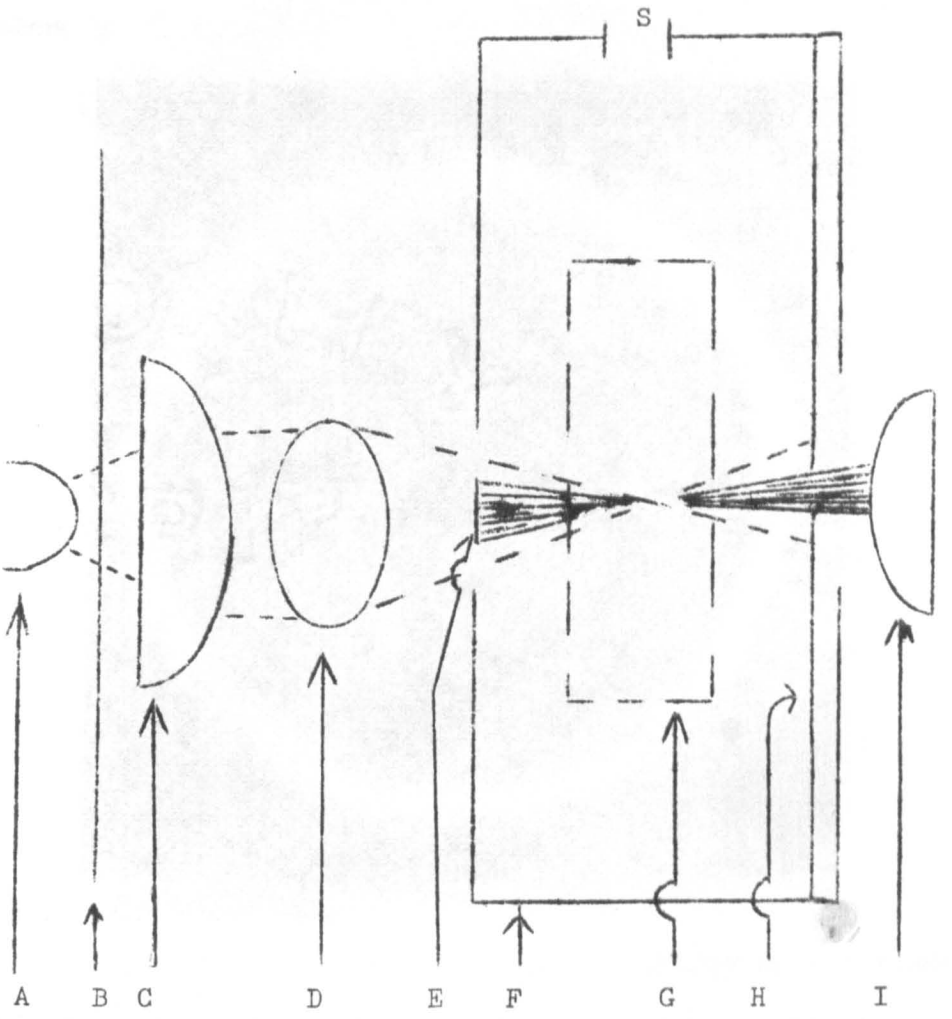


Fig.15 The size distribution of 420 particles determined by microscopy.

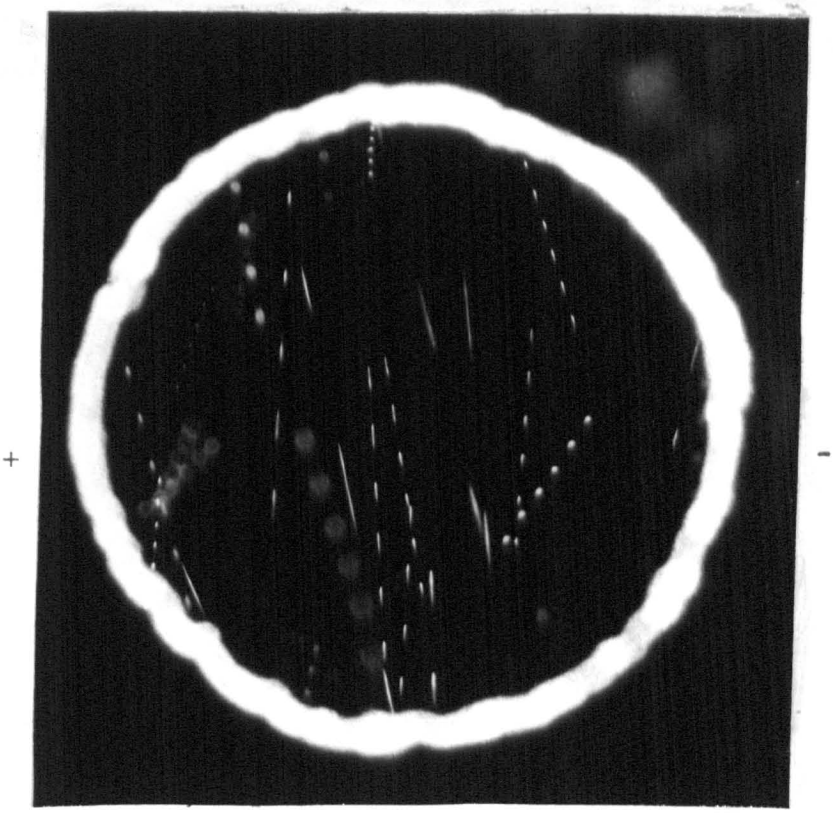


A - Light
B - Chopping disc
C - Condenser
D - Lens
E - Light baffle 1
F - Sedimentation chamber
G - Electrodes
H - Light baffle 2
I - Camera
S - Particle entrance slot

Fig. 16 The Dark Field Ultramicroscope.

Light from a slide projector (300 watts quartz halogen) is 'chopped' by the rotating 'chopping disc', to produce stroboscopically photographed tracks. After the disc the light is focussed into a cone the focal point of which is between the electrode faces. Light baffle 1 produces the dark cone and light baffle 2 reduces light which might otherwise reach the camera. Particle tracks appear as well defined images crossing a dark background disc surrounded with a circle produced by the small amount of incident light passing baffle 2.

An example of the tracks photographed in the dark field instrument is shown in Photograph 14.



Photograph 14.

Sub - micrometre particles may be measured but, as Kunkel and Hansen found in their analysis of dust particles, there is a cut off at about 10 μm radius due to the rapidity at which larger particles fall through the small area of view.

To measure the tracks recorded on film negatives each negative, suitably labelled, was mounted in a transparency plastic frame and put into a slide projector which had been secured to a bench and levelled with a spirit level . The image was projected on to an enlarger masking frame covered with mm squared paper and mounted vertically on a second bench horizontally and directly opposite to the projector. By projecting the image of the graticule the scale of magnification was determined and the various measurements required from track negatives could be quickly obtained simply by moving the vertical and horizontal arms of the masking frame.

Calculations from the measurements were made thus:-

Let V_x = horizontal velocity due to E field, V_y = vertical velocity due to gravity (terminal velocity) v = number of light flashes per second, M = magnification, N = No. of intervals in trace, X = horizontal displacement, Y = vertical displacement.

$$V_x = \frac{X\,v}{M\,N} \text{ ms}^{-1} \qquad V_y = \frac{Y\,v}{M\,N} \text{ ms}^{-1}$$

If s = distance and t = time then, $V = \frac{s}{t}$

$$s = \frac{X}{M} \quad \text{or} \quad \frac{Y}{M}$$

$$t = \frac{N}{v}$$

$$V = \frac{\frac{X}{M}}{\frac{N}{v}}$$

$$V = \frac{X\,v}{MN} \text{ m s}^{-1}$$

Assuming Stokes' Law applies, which is for laminar flow and spheres.

Particle radius $a = \left(\frac{9\,\eta\,V_y}{2\,\rho\,g}\right)^{\frac{1}{2}}$

$\eta = 18 \times 10^{-6}$ Nsm^{-2}

$\rho = 2165$ kg m^{-3}

$g = 9.81$ m s^{-2}

Particle charge $q = \frac{6\pi\,d\,a\,V_x\,\eta}{E}$

d = dist. between electrodes = 0.002m

E = voltage across electrodes

The size distribution of particles obtained are displayed in Fig. 17.

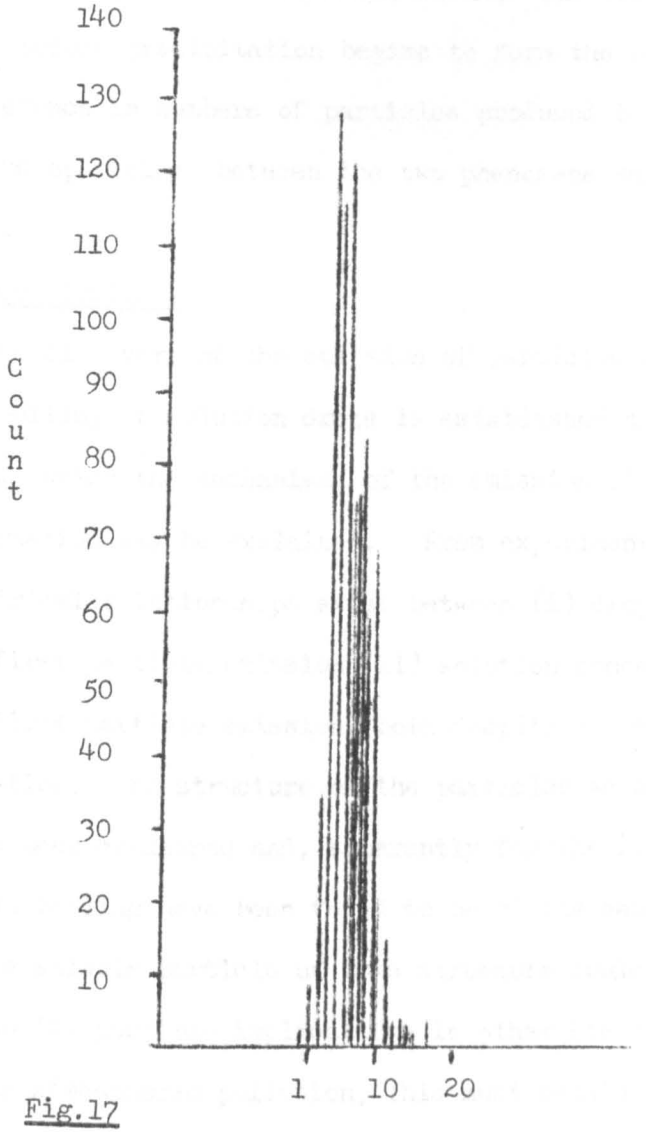


Fig.17

Particle radius 10^{-6}m (760 values)

(rounded values 0.5 up)

Out of all particles measured only one was found in the sub micrometre range and that was a particle of radius 0.9μm. The explanation for the difference in radii of particles from Leidenfrost drops in comparison with those from flash boiling (e.g. Woodcock & Spencer) would seem to lie in the mechanism of particle production and the solution concentration. In the case of Leidenfrost drops the solution from which droplets originate is already at precipitation point when they begin to form their outer shell. But in the case of flash boiling the solution is at its initial concentration, is thrown off rapidly in great numbers of tiny droplets due to frothing, bursting

bubbles and 'explosive' release of steam, and evaporation of water has to occur before precipitation begins to form the outer particle shell. The difference in numbers of particles produced is due to the different mechanisms operating between the two phenomena which produce solution droplets.

6.0.9 Conclusions.

The discovery of the emission of particles from the Leidenfrost form of boiling of solution drops is established as a reproducible process in which the mechanism of the emission of the particles and their formation may be explained. From experiments it has been found that empirical relationships exist between (i) drop volume and the time to first particle emission (ii) solution concentration to the time of first particle emission, both despite the haphazard nature of the situation. The structure of the particles as a hollow crystalline shell has been explained and, apparently for the first time, the particles from flash boiling have been found to be of the same structure. Although a soluble particle of this structure could be considered with respect to its possible implications in other fields, such as raindrop nuclei, or atmospheric pollution, this must remain for some future date and it now remains to investigate the electrical properties of the particles found to be produced from Leidenfrost drops.

6.0.10 Summary of chapter 6.

1) If a saline solution is subjected to the Leidenfrost form of boiling evaporation of water will take place until the precipitation concentration of the solute is reached, atwhich point a crystalline skin will precipitate out on the underside of the drop due to maximum evaporation from there causing supersaturation of the solution and consequent precipitation. The existance of this crystalline skin will shut off the vapour layer support and cause the drop to fall on to the hot surface.

2) On contacting the hot surface crystalline decrepitation will occur and result in the precipitated skin and some of the drop solution from

the base of the drop, and thereby supersaturated, to be laterally expelled from beneath the drop. This material in the form of droplets will produce particles and its expulsion from the drop is the particle emission mechanism. It is random mechanism in that neucleation of the crystalline material is a random process but it is reproducible in that it has never failed to occur.

3) The first emission of droplets, that is the first emission mechanism operating for each new drop is most likely to occur when the drop reaches a smaller volume V_2 such that $V_2 = \frac{V_1 A_1}{A_2}$ where V_1 = initial volume

A_1 = initial solution concentration

A_2 = precipitation concentration

4) The mean time at which the first particle emission mechanism will operate for each new drop has been found to be:-

$$t_p = 0.8 \quad (1.35 \times 10^8 V_1)^{\frac{1}{2.4}} - (1.35 \times 10^8 V_1 A_1 A_2^{-1})^{\frac{1}{2.4}} \quad s$$

5) The average number of particle emissions from a 1 ml drop of 3.5% Na Cl solution is 1,444

6) There is only a very slight correlation between the number of particle emissions and the duration of time during which particles are being emitted, due to the random behaviour of the emission mechanism.

7) The average number of particles per emission is 450

8) The particles are spherical, hollow and have an outer crystalline shell which has no apparent cubic structures. Particle wall thickness is not uniform and cubic crystals may be found. Each particle has at least one hole where vapour or entrapped solution escaped as increasing internal pressure due either to evaporation or continued crystallization acted at a weak section of the wall. Solid particles from the disruption of the crystalline skin are not found due to the redissolution of this in the ejected solution.

9) Particles produced by flash boiling and from a spray gun have the same structure as those from Leidenfrost boiling.

10)Particles from Leidenfrost boiling of saline solution range in size from 1μm to 210μm in radius with the majority having a radius of 3μm to 10μm.

11) The total number of such particles emitted from a 1 ml drop of 3.5% Na Cl solution is 6×10^5

Chapter 6 References.

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7.0.0 The electrical properties of Leidenfrost drops and associated particles.

(Unless otherwise stated all drops are of 1 ml volume and 3.5% $NaCl_{aq}$.)

7.1.0 Introduction.

It has been mentioned (4.3.3) that each particle emission generates electricity and this fact has been used to count the number of particle emissions. The fact that a drop of solution undergoing Leidenfrost boiling has been shown conclusively to generate electricity resolves, in the affirmative, a two centuries old controversy as to whether this was the case or not. H.B. de Saussure in 1786 (2.2.2) stated that no charge was produced by this form of boiling. Peltier contradicted this in 1841 (2.2.7). But Blanchard (1964)(3.2.0) commented that he had observed no current flow from a Leidenfrost drop and he in turn was contradicted by Pounder (1972) (3.3.1 ref 7) who mentioned that charge was produced. This investigation confirms not only that electricity is generated but that it is so in a very interesting manner by the production of a charged particulate cloud.

The pulses of charge produced may be analysed for information relating to the particle emission mechanism, the average charge on one particle and the vapour layer thickness. The distribution of charge per particle has been obtained from the ultramicroscope described in the previous chapter.

In chapter 10 some speculations will be made on which charging mechanisms may be operating to produce charge in the Leidenfrost solution drops and particles and to help with this some experiments were made on heated surface material other than metals.

Investigation of the electrical properties of the Leidenfrost drops began with a re-examination of the Tyndall demonstration of the insulating properties of the vapour layer supporting the drop.

7.2.0 The resistance of the supporting vapour layer.

In 1870 Tyndall had, on a suggestion of Poggendorf, demonstrated that the vapour layer was an insulator (4.1.2). In an experiment similar to that of Tyndall but using a Keithley electrometer, set up on its resistance range, connected to a chart recorder (Fig.1) it was found that the resistance of the layer varies.

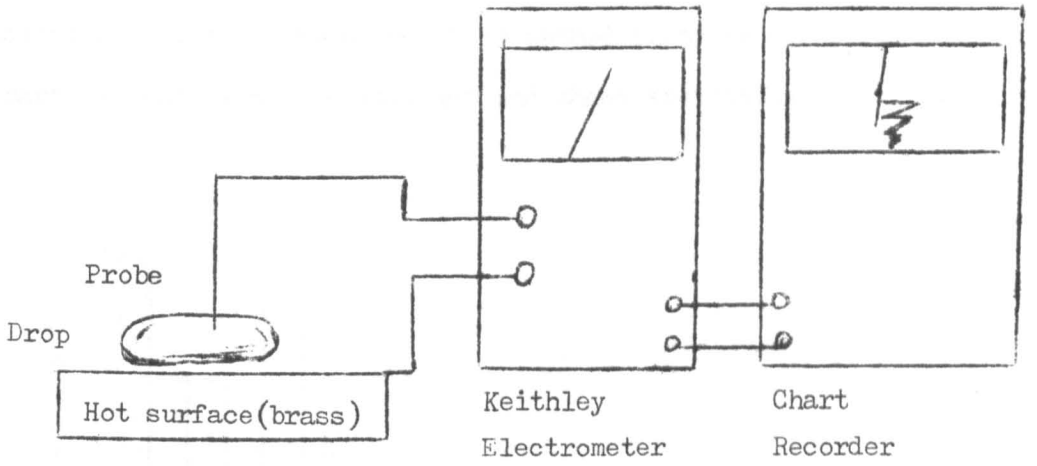


Fig.1 Vapour layer resistance apparatus.

The maximum value was 2.3×10^9 ohms, the average resistance was about 2.5×10^8 ohms and the minimum was 0 ohms. Apart from obtaining these values no further investigation was undertaken but evenso from this information an important fact emerged in that the vapour layer resistance was minimum at particle emission. This is consistent with the mechanism proposed in chapter 6 since when the crystalline skin has formed and so shut off the vapour layer support, the drop touches the hot surface - in effect short circuiting the apparatus of Fig.1.

7.2.1 Recording electrical pulses.

Charge magnitudes of 10^{-10}C generated by each particle emission was first measured by locating a probe in the drop (as in Fig.1) and taking direct readings from an EN 50 electrometer (Walden Precision Instruments). These results were verified by a second method employing a chart recorder fed, via a FET input operational amplifier (Philbrick/ Nexus 1009) in line with a 741 operational amplifier. A less complicated

but reliable third method of measuring and recording charge employed the circuitry of Fig 1 but with the electrometer set to measure charge. (Some word of explanation is perhaps necessary as to why three methods of measuring charge were involved when one, the third, is so obviously easy and reliable. The first two were employed in experiments carried out in the author's laboratory and the third was used as part of the facilities of the University of Southampton, Department of Applied Electrostatics). From the third method fifty values of charge per particle emission were obtained and these are displayed in Fig.2.

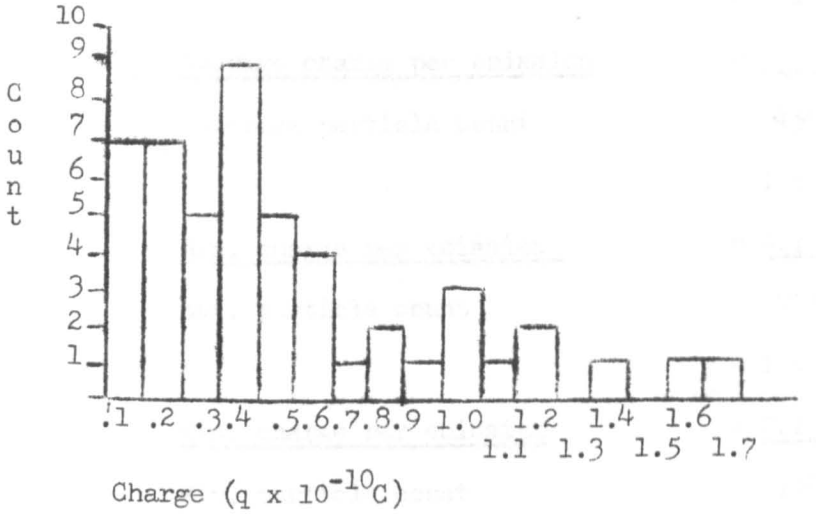


Fig.2 Charge per particle emission.

The average charge per particle emission = 0.5 x 10^{-10}C and the minimum charge = 0.1 x 10^{-10}C. The different values in charge per particle emission could arise from more particles per emission in some instances thus carrying on them an overall larger quantity of charge. The information gained on the charge produced per particle emission was used with the information on numbers of particles produced per emission (6.0.5) to obtain an estimate of the charge per particle.

7.2.2 Charge on a particle - first estimates.

The information relating to the number of particles and the magnitude of charge produced in a particle emission were not obtained simultaneously therefore several comparisons were made, as follows, to make an estimate of the magnitude of charge per particle.

$$\frac{\text{Average charge per emission}}{\text{Max. particle count}} = \frac{0.5 \times 10^{-10}}{708}$$

$$= 7 \times 10^{-14} \text{C particle}^{-1}$$

$$\frac{\text{Average charge per emission}}{\text{Min. particle count}} = \frac{0.5 \times 10^{-10}}{198}$$

$$= 2 \times 10^{-13} \text{C particle}^{-1}$$

$$\frac{\text{Average charge per emission}}{\text{Average particle count}} = \frac{0.5 \times 10^{-10}}{450}$$

$$= 1 \times 10^{-13} \text{C particle}^{-1}$$

$$\frac{\text{Min. charge per emission}}{\text{Max. particle count}} = \frac{0.1 \times 10^{-10}}{708}$$

$$= 1 \times 10^{-14} \text{C particle}^{-1}$$

$$\frac{\text{Min. charge per emission}}{\text{Min. particle count}} = \frac{0.1 \times 10^{-10}}{198}$$

$$= 5 \times 10^{-14} \text{C particle}^{-1}$$

$$\frac{\text{Min. charge per emission}}{\text{Average particle count}} = \frac{0.1 \times 10^{-10}}{450}$$

$$= 2 \times 10^{-14} \text{C particle}^{-1}$$

The magnitude of charge on an individual particle is 10^{-14}C to 10^{-13}C.

7.2.3 Pulse shape.

The pulses produced by particle emissions have a characteristic shape shown in Fig 3 by superimposing pulses from a chart record. These pulses were recorded in the early stages of particle emission from drops when each emission is well spaced in time. When the drop has been emitting particles for some time the emissions are so close

together that charge on the drop begins to accumulate and ultimately reaches a value of - 10^{-5}C.

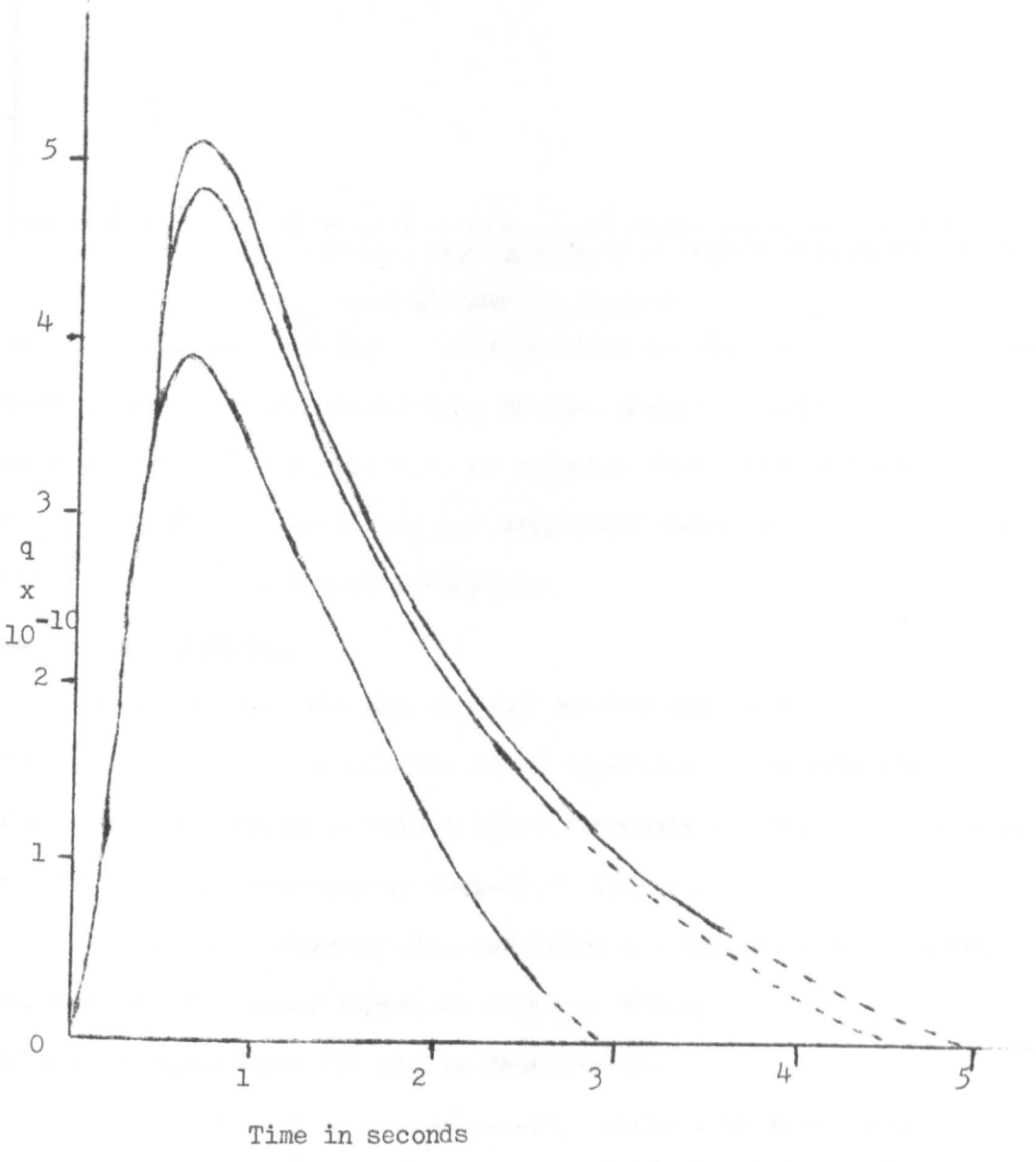
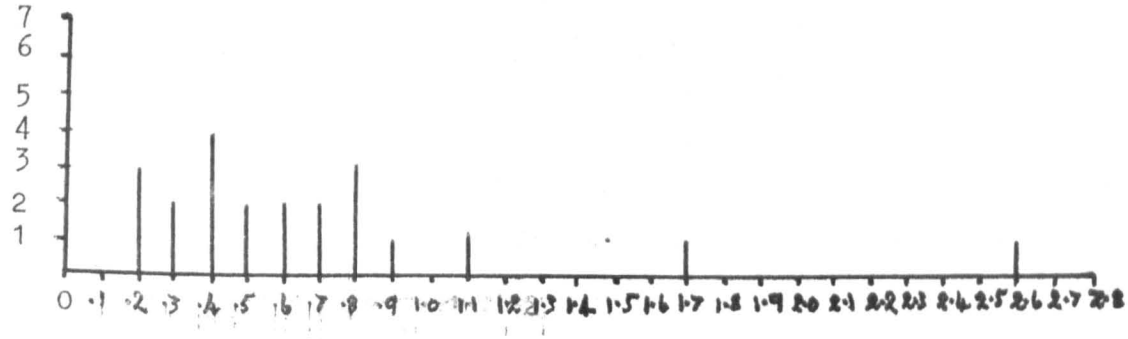


Fig.3 Charge on drop at each particle emission. (q is negative C) .

Each pulse rises to a single maximum value of charge and then falls to a minimum. It is assumed that the rise time corresponds to the duration of charge generation and the fall is due to the decay of charge through the vapour layer. The decay times of twenty two pulses are displayed in Fig 4.

Fig.4 Decay times of electrical pulses (rounded values).



Decay time to zero in seconds

The pulse curves used for Fig.4 were measured on the chart record of charging and were those which distinctly fell to zero charge in order to obtain reasonably accurate values of decay time i.e. as distinct from the three used to illustrate pulse shape in Fig.3 which did not completely decay before the drop was 'recharged' by the next particle emission.

Vapour layer thickness.

By assuming that the drop and hot surface separated by the vapour layer may be regarded as a parallel plate capacitor it is possible to calculate possible values of vapour layer thickness (d) for comparison with those obtained by photography in chapter 5 (5.1.2).

The 'capacitor' charges when particles are emitted and the charge decays, through the vapour layer, as shown in Fig.4.

Values of capacitance (C) may be determined:-

$$t = \frac{C}{R} \quad s \text{ ---------(1)}$$ where t is decay time s, R is resistance of layer

then $$C = \frac{t}{R} \quad F \text{ --------(2)}$$

and since $$C = \frac{\epsilon_o \epsilon_r A}{d} \quad F \text{ --(3)}$$ where d = layer thickness, $\epsilon_o = 8.854 \times 10^{-12}$, $\epsilon_r = 1$, A = area of drop base

then $$d = \frac{\epsilon_o \epsilon_r A}{C} \quad m \text{ ----(4)}$$

By putting values of decay time and vapour layer resistance in (2) and the values of capacitance so obtained into (4) values for d the thickness

were found to be in the order of 10^{-3} to 10^{-2}mm, (sample values of d = 0•003mm, 0•004mm, 0•01mm, 0•04mm, 0•09mm). The values of the order of 10^{-2}mm compare well with those estimated in chapter 5 but there are obviously differences between the two methods which may be due to the fact that the photographic method views only the part of a drop edge at a particular moment in time whereas the decay time/capacitance will involve all the layer over a period of time during which the drop is in motion and a solid salt layer is forming.

7.2.4 Distribution of charges on individual particles.

The method of calculating the charge on an individual particle was given in 6.0.8 (relating to the dark field ultramicroscope). The distribution of charge per particle is displayed in Fig.5 (N.B. on particle radii within the range of the ultramicroscope).

The charge magnitude per particle obtained in section 7.2.2 of 10^{-14}C to 10^{-13}C obtained from the charge on the drop per particle emission was therefore determined for all particle sizes and not only for those within the range of the ultramicroscope. It seems reasonable to speculate that larger particles, not registered by the ultramicroscope, might be carriers of greater quantities of charge. Some evidence in support of this speculation is given by Fig 6 showing charge to radius.

An individual particle may have positive or negative polarity or no charge at all but the nett charge on all particles is positive. Observations of drop polarity during particle emission show that the electrometer will indicate both + and - on either side of zero, the opposite polarity having been carried off on particles. Of course the charge measured by the electrometer is nett charge and from this it is possible to gain some idea of the nett charge on a particle cloud. An example is given from four drops - in Table 1 :-

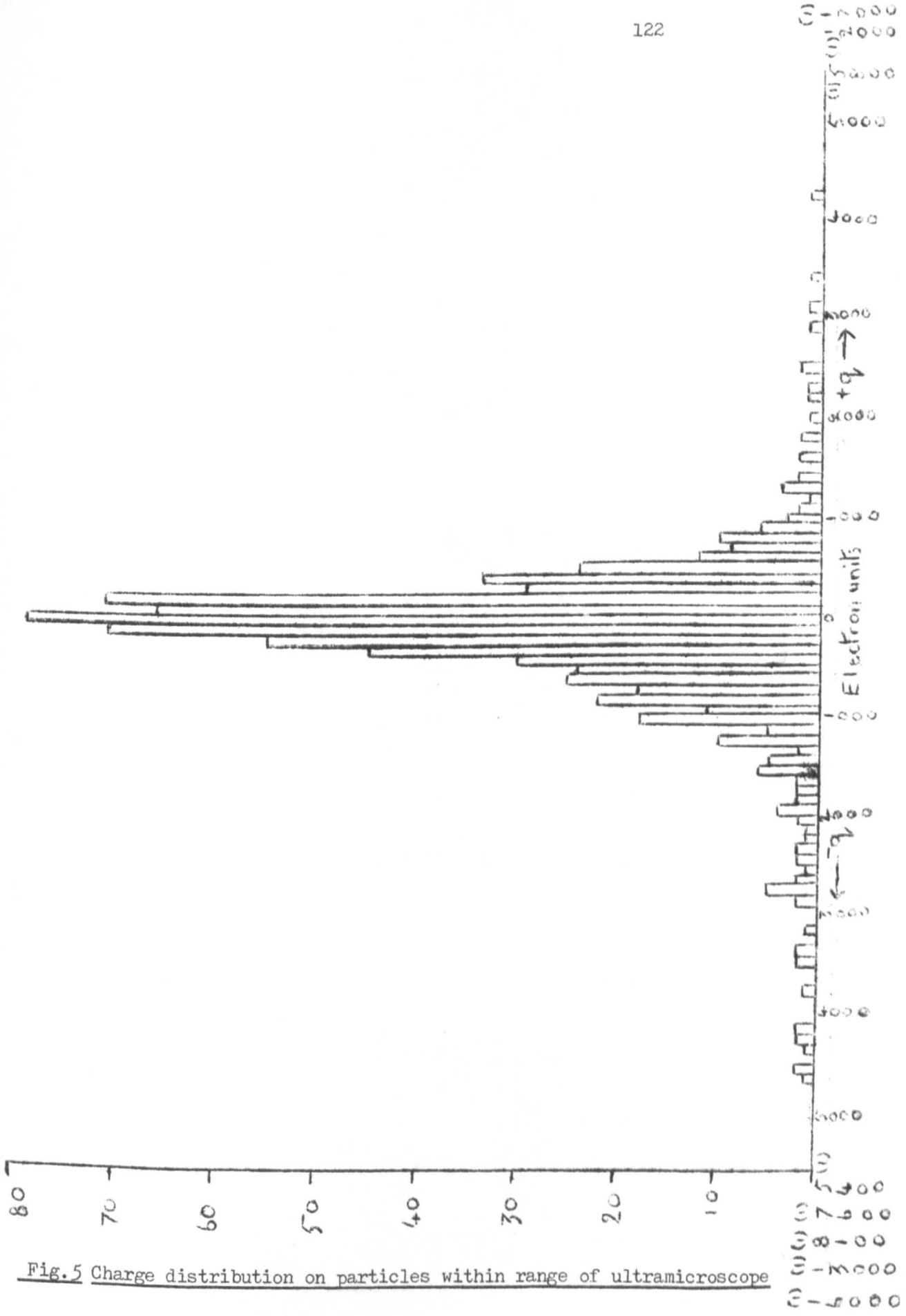
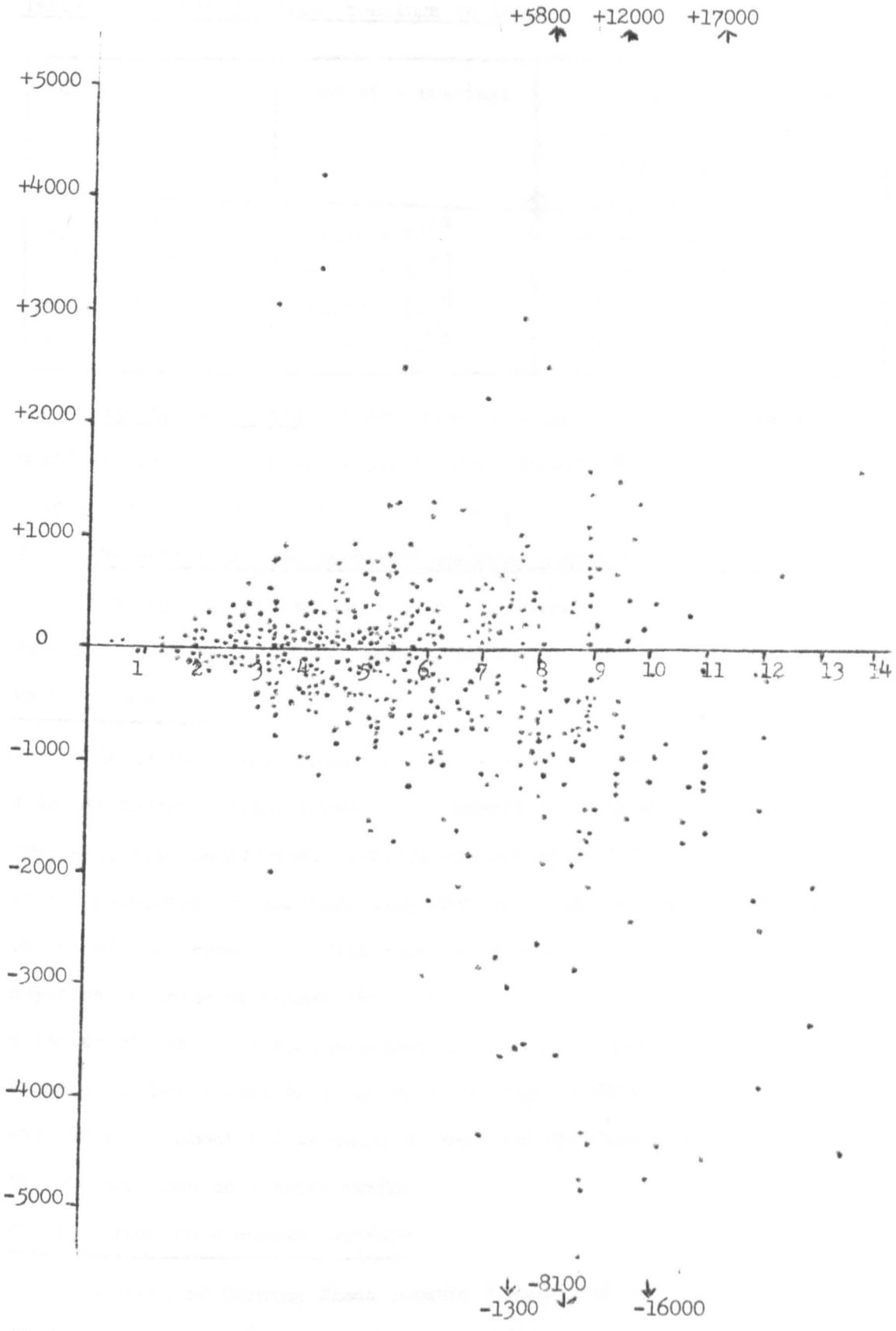


Fig.5 Charge distribution on particles within range of ultramicroscope



Vertical axis: charge in electron units

Horizontal axis: radius in micrometres

Fig.6 Particle charge to radius.

Table 1 Values of charge readings on drops.

Sum of + readings	Sum of - readings	Difference: the equal and opposite polarity having been carried away on particles
$+0.5 \times 10^{-9}$C	-1.42×10^{-9}C	-0.92×10^{-9}C
$+0.25 \times 10^{-9}$C	-0.51×10^{-9}C	-0.26×10^{-9}C
$+0.21 \times 10^{-9}$C	-0.53×10^{-9}C	-0.32×10^{-9}C
$+0.26 \times 10^{-9}$C	-0.40×10^{-9}C	-0.14×10^{-9}C

The charge to mass ratio of particles of 10μm (this being the average particle size found in particulate cloud studies (Bright 1977[1]) ranges from 1.9×10^{-4} to 2.0×10^{-3} C kg^{-1}.

7.2.5 The effect on drop charge of changing heated surface material.

To provide information for use in chapter 10 $Na\,Cl_{aq}$ drops were set up on $Na\,Cl_s$ and a ceramic surface.

$Na\,Cl_{aq}$ on $Na\,Cl_s$

Solid Na Cl was heated from above with a Bunsen burner until a smooth molten surface about 3 cm diameter was produced. A Leidenfrost drop was, with considerable difficulty, set up on this surface. The charge generated by particle emissions was measured with an immersed probe and electrometer. With each particle emission the drop had a nett negative polarity of charge the magnitude of which -2×10^{-11}C was a factor of ten below that measured from drops on metal surfaces. Since a red hot molten Na Cl surface was very difficult to maintain only drops of about 0.2 ml could be used but the charge was a magnitude of ten less than on a metal surface.

$Na\,Cl_{aq}$ drops on a ceramic surface

A sheet of Corning Glass ceramic (capable of withstanding a thermal shock of 900°C) was heated on a boiling ring and drops were set up on it. As with $Na\,Cl_s$ (surface) the charge produced on each particle emission was less, by a factor of ten, than that produced by a drop on

a metal surface.

Particle emission charges on drop:-(Ceramic surface)

Mean of 20 values = 1.8×10^{-11}C

Na Cl_{aq} drops on brass on ceramic.

A sheet of brass was heated and placed on a sheet of ceramic and drops set up. With one exception (-2.0×10^{-11}C) the magnitude of charge was that usually found from a drop on a metal surface:

Mean of 9 values = 1.75×10^{-10}C

It is demonstrated that the material of the heated surface has some bearing on the quantity of charge produced and this will be taken note of in chapter 10 when speculations are made on contributory charging mechanisms.

7.3.0 Conclusion and summary.

After two centuries since it was first examined from an electrical standpoint the Leidenfrost boiling of saline solution is conclusively proved to generate electricity. The solution in the form of a drop is supported on a vapour layer the resistance of which, though normally high, is variable and falls to zero on each emission of electrically charged particles. The electrical properties of these particles are summarised in Table 2 below. It has been demonstrated that the material constituting the heated surface affects the quantity of charge produced. By assuming that the drop, layer and surface are of the structure of a parallel plate capacitor it has been possible to offer supporting evidence for values of vapour layer thickness obtained in chapter 5. The pulses produced by a particle emission have been examined. The amount of charge carried by a particle was estimated and a charge per particle distribution obtained from the dark field ultramicroscope.

Table 2 Summary of electrical properties of Leidenfrost drops.

Leidenfrost drops of saline solution produce electricity.
A Leidenfrost drop has a net negative polarity - the opposite polarity of charge is assumed to be on the particulate cloud.
Average charge per particle (Na Cl) all radii = 10^{-14}C
Charge on 10μm particles (Na Cl) = 10^{-16}C to 10^{-17}C
$\frac{q}{m}$ ranges from 1.9×10^{-4} to 2.0×10^{-3} C kg^{-1}
Charge per particle increases with particle radius.
A net polarity is found on the particle cloud.
Changing the heated surface material from a metal to a ceramic decreased charge produced by a factor of ten viz (10^{-10}C to 10^{-11}C)

Chapter 7 References.

1. A.W. Bright, private communication, 1977.

8.0.0 Exploratory investigations of some aqueous solutions.

8.1.0 Introduction.

The thesis presented so far has been restricted to the aqueous solution of Sodium Chloride for the simple reason that the investigation arose from the earlier studies of saline contact charging. (Presented in chapter 3). The majority of the volcanoes of the world are situated on the shores of seas and oceans or emerge from them as islands (Francis 1976 [1]). For this reason Na Cl may be claimed as being an important component in aqueous solution contact charging. A cursory survey reveals it to be present in inland waters - a list of Mineral Baths and Wells for Europe in 1898 [2] shows that in 208 Spas 112 (54%) had Na Cl in the water; the more recent 1971 hydrogeochemical survey of Derbyshire groundwaters [3] sampled 116 water sources all of which were found to have Na Cl present. Since crater lakes and other water sources exist in the vicinity of volcanoes (see chapter 2) some consideration must be given to other substances able to precipitate crystalline material from an aqueous solution.

If a serious case for continued study of aqueous solutions in contact with heated surfaces generating charge is to be substantiated then the important questions must be posed:

(i) Do aqueous solutions other then Na Cl_{aq} produce electricity ?

(ii) If the answer is in the affirmative do they produce charge by the three forms of boiling now known to generate charge and particles, namely, Flash Boiling, Blanchard Effect, Leidenfrost Phenomenon ?

In seeking to answer these questions the aim was to obtain a simple yes or no with some supporting evidence. If affirmative answers were obtained then the field of study of boiling aqueous solution charging contributory to volcanic lightning would be open for future continued study. As this chapter's title states the results are exploratory and the chapter, if it is to be of value, is open ended and a source of ideas and objectives

for a wider study of volcanic lightning and the contributing aqueous solution charging.

8.2.0 The Polarity and Maximum Charge produced by 1 ml volumes of various aqueous solutions boiling on heated surfaces.

Solutions were either made up from laboratory chemicals or volcanic and other natural sources. This thesis has concentrated on the Leidenfrost form of boiling but in this exploratory chapter two other forms of boiling, namely, Blanchard effect (abbreviated BE) and Flash Boiling (abbreviated FB) will also be considered.

Some trials with different materials for surfaces and charges produced by some decrepitating crystals were also tried with a view to further investigations at some future date. The results of the varied exploratory experiments are given in tables 1 to 6.

Table 1 (All drops 1 ml on a Stainless steel surface).

Solution	Max Q in C	Form of boiling	Comments
$CuSO_4$	-0.12×10^{-7} -0.13×10^{-8}	BE FB	Two drops tried in each case
I	$+0.3\times10^{-9}$ $+0.5\times10^{-9}$	BE FB	Three drops BE gave same values. Three drops FB gave slightly different values but of same magnitude.
NaI	-0.1×10^{-7} -0.2×10^{-9}	BE FB	Two BE same values Two drops FB same magnitude
K Br	-0.1×10^{-7} -0.3×10^{-8}	BE FB	Several drops BE & FB same order of magnitude. Conc. 3.5%
$Na\ SO_4$	-0.3×10^{-8} -0.3×10^{-8}	BE FB	
Na Cl	-0.2×10^{-7} -0.1×10^{-7}	BE FB	
Sea water	-0.3×10^{-9} -0.1×10^{-8}	BE FB	Sample from Anglesey
Aq.sol. Pumice	-0.12×10^{-8} $+0.9\times10^{-9}$	BE FB	Powdered grey pumice was mixed with distilled water and allowed to settle the clear solution was used.
Aq.sol. Vesuvius	-0.1×10^{-8} -0.12×10^{-8} $+0.1\times10^{-8}$	BE FB FB	Fine reddish dust from Vesuvius was used to obtain a solution as with pumice above. + polarity observed on one of six drops.
Buxton water	-0.4×10^{-7} -0.1×10^{-8} $+0.12\times10^{-8}$	BE FB FB	Sample of water from deep thermal spring Buxton,Derbys.,several reversals of polarity observed;solution complicated
Potassium Permanganate	-0.6×10^{-8} -0.7×10^{-8}	BE FB	
Commercial 'mineral' bath salts	-0.2×10^{-9} $+0.1\times10^{-7}$ $+0.1\times10^{-7}$	LD BE FB	Particle emission observed

Although at some future date it may be possible to correlate the charge magnitude to either the chemical properties of the solution and/or to the form of boiling there is no obvious explanation for the reversal of charge polarity. In the cases where this occurs because different forms of boiling were in operation some correlation may be envisaged but such an explanation could not be applied to solutions exhibiting a particular form of boiling but during which a reversal of charge polarity was observed.

Table 2 Observations of the behaviour of some aqueous solutions exhibiting the Leidenfrost phenomenon.

NaI	Produces particles in the same way as Na Cl but with a tendency to make more 'dramatic' emission noise or crackling. $Q = -5 \times 10^{-10}$C.
K Br	Particle emission with violent drop break up on each emission. $Q = -3 \times 10^{-10}$C.
I	Drop shrinks slowly in size becomes cloudy and crystals sometimes form on drop surface which explodes with a loud "Crack!" $Q = -5 \times 10^{-10}$C. Iodine is extremely difficult to work with.
$CuSO_4$	Drop seems to catch surface often. Particles may be emitted. $Q = -5 \times 10^{-10}$C.
Potassium Permanganate	Erratic behaviour with apparent particle emission, somewhat like Iodine. $Q = -3 \times 10^{-10}$C

Table 3 Aqueous solutions on different metal surfaces (Leidenfrost drops).

Stainless Steel	
Na Cl	Electrometer + & - either side of zero.
Na I	Electrometer + & - either side of zero but more on + .
$CuSO_4$	Similar to Na Cl but more - .
I	High residual charge inconsistent results.
Copper	
Na Cl	Electrometer either side of zero but mostly + falling to 0 on particle emission.
NaI	Electrometer mainly + side of zero.
$CuSO_4$	Electrometer either side of zero.
I	High residual charge +. Erratic behaviour results inconsistent.

Table 4 As Table 3 but with charge values.

Brass	
I	Drop becomes cloudy. Steady charge build up to $+10^{-10}$C. Pulsesof 10^{-11}C approx. Some particle emission. Qmax. $+3 \times 10^{-10}$C.
Pumice	Nearly clear solution from above settled out grey pumice in distilled water. + & - 10^{-11}C ultimately rising to $+10^{-10}$C.
Vesuvian dust	Clear solution from above settled dust + 3×10^{-10}C.
Na Cl	-10^{-10}C
Na I	$+3 \times 10^{-10}$C.
Copper Block	
Na Cl	Clean surface slightly tinted with oxide colours. Initially low charge but as heavy oxide layer built up final $Q = -2 \times 10^{-10}$C
Na I	Low charge + & - 10^{-11}C.
Stainless Steel	
Na Cl	Increasing in steps 10^{-11}C to final $Q = -3 \times 10^{-10}$C.
Na I	Increasing in + steps 10^{-11}C to final $Q = +2.3 \times 10^{-10}$C.

All solutions used were aqueous either prepared by adding crystals to distilled water or obtained from natural sources such as thermal springs. It is known that many crystals decrepitate and it was decided to find out if charge was produced as this occurs. The results obtained are displayed in tables 5 and 6.

Table 5 Charges produced by some crystals decrepitating on hot surfaces. Electrometer connected between hot surface and earth.

Brass	
Na Cl	Large & Medium crystals -5×10^{-10}C
K Br	Large crystals (0.25 cm side) $+5 \times 10^{-10}$C.
Alum	Large & Medium crystals. No decrepitation, no charge.
$FeSO_4$	Small crystals, same results as alum.
Pot.Permag.	Small crystals violent decrepitation, electrometer off scale $+5 \times 10^{-10}$C.
$CuSO_4$	Slow loss of water of crystallization, no charge.
Na Cl	Violent decrepitation -5×10^{-10}C.
Cast Iron	
Na Cl	Violent decrepitation -5×10^{-10}C.
K Br	Less decrepitation than on brass $+4 \times 10^{-10}$C.
Copper, heavy oxide due to heating.	
Na Cl	Violent decrepitation, off scale -5×10^{-10}C.
K Br	Little decrepitation $+10^{-10}$C approx

Table 6 Crystals were heated in a covered dish on a boiling ring and dropped into cold distilled water in a stainless steel dish on an insulated tripod stand connected to an electrometer.

Na Cl	Violent decrepitation, charge in excess of -5×10^{-10}C.
K Br	Violent decrepitation, charge in excess of -5×10^{-10}C.
(Potassium Bromide definitely changed polarity by this method compared to decrepitating on a hot metal surface.)	

8.3.0 Concluding comments.

The three forms of boiling and crystalline decrepitation of various materials are demonstrated to produce charge. It has also been found that some solutions produce particles. The laboratory trials substantiate the idea of investigating aqueous solutions associated with volcanic lightning for solutions which precipitate a crystalline solute subject to decrepitation. Each solution would need to be investigated with respect to particle size and charge distribution.

There is some need for field investigations of boiling solutions and analysis of water sources in addition to refined laboratory investigations to resolve the question of polarity reversal with certain substances as well as to attempt to correlate various chemical and physical parameters when aqueous solutions are subjected to the various forms of boiling.

Chapter 8 References.

1. P. Francis, Volcanoes, 1976, Penguin Books.

2. J. M' Gregor-Robertson, The Household Physician,2nd edition,1898, Blackie & Son.

3. W.M. Edmunds, Hydrogeochemistry of groundwaters in the Derbyshire Dome with special reference to trace constituents, 1971,NERC, Inst. Geological Sciences,H.M.S.O..

9.0.0 A discussion of charging mechanisms and a review of some examples of charging processes.

9.1.0 Introduction.

A profusion of terms exist relating to electrostatic charging due in part to the nature of the subject and to the time and place in history of individual investigators. For the purposes of this chapter two terms will be used:-

(i) Charging process to refer to a phenomenon which results in the appearance of charge.

(ii) Charging mechanism to describe the action which brings about a redistribution of electrons in materials and which is thereby the origin of the charge which appears in a process.

In the review of processes section a way of understanding the relationship between the two terms will be to think of each process as an element of a set with a many - to - one relationship to the mechanism. The characteristic property of a 'process set' will be its charging mechanism.

E.g. { Droplets from bursting bubbles, waterfalls, Spray from transported in liquids, Solid particles } (Characteristic charging mechanism - Double layer).

Simple classification of this kind is fraught with problems largely due to lack of experimental reproducibility which is itself affected by the presence of impurities, surface preparation problems and the state of knowledge appertaining to the structures of liquids - particularly water and electrolytes - and the physics and chemistry of surfaces and interfaces.

From Gilbert (1600) to Lenard (1892) 'electricians' sought a mechanism to explain all charging processes. The author has recently reviewed these early attempts [1]. This review will not be repeated here since the present object is to examine the current understanding in order to suggest, in the next chapter, those mechanisms which may be present in the case of Leidenfrost drops. A most pessimistic

atmosphere prevailed when Loeb (1945)[2,3] wrote of a 'most unsatisfactory array of discordant, often non-reproducible and confusing results, whose theoretical interpretation is quite hopeless' and Harper (1957)[4,5] in a similar frame of mind stating that, 'these manifestations give little indication of what is causing them: one is seldom sure whether a particular process will give charging or not, and often, when it does, what the sign of the charging will be'.

As interest in electrostatics has grown over the last decade more processes are being discovered and modern 'electricians' seek a variety of mechanisms to explain processes. As yet not all processes can be conveniently located as an element in a set with one characteristic charging mechanism, in part due to the complexity of action in the operation of the process as well as the problem at the present time of being unable to state definitely how electrons are physically redistributed in a charging mechanism. Bearing this in mind the first section of this chapter will be a discussion of the two predominant charging mechanism hypotheses followed by a review of some processes using these and, in the following section, some examples of processes which cannot be conveniently related to a characteristic mechanism and which are the subject of exciting controversy and ongoing investigation. Indeed the material of the entire chapter is subject to exciting controversy and ongoing investigation!

9.2.0 Solid-solid contact charging mechanism.

An electrically neutral atom of an element has a positive nucleus surrounded by negative electrons. The electrons occupy discrete energy levels governed by their fundamental properties of charge, mass, spin and quantum of action. In the crystal lattice of a solid the proximity of neighbouring atoms causes these energy levels to be widened into energy bands and the probability of an electron having a particular energy is governed by Fermi-Dirac statistics. Unlike Maxwell-Boltzmann statistics, which place no restriction on the number of particles

occupying particular energy levels, the Fermi-Dirac probability function

$$f(E) = \frac{1}{1 + \exp\left\{\frac{E - \zeta}{kT}\right\}}$$

incorporates the effects of Pauli exclusion. A typical distribution of the probability of electrons of particular energies being located in particular levels is as shown in Fig.1.

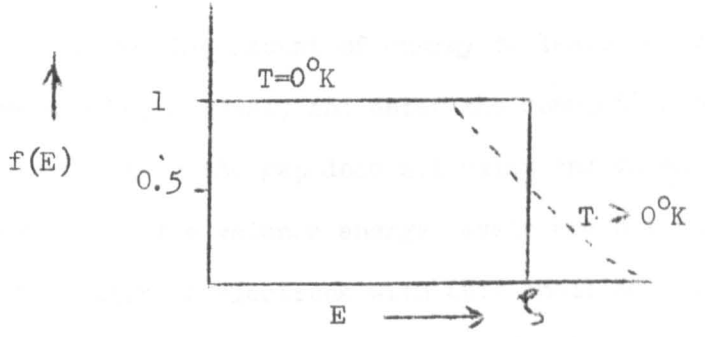


Fig.1 Fermi-Dirac probability function at $T = 0^{\circ}K$ & $T > 0^{\circ}K$

The term ζ is called the Fermi level and is the energy limit above which electrons will not be accomodated at absolute zero of temperature ($T = 0^{\circ}K$). At temperatures above absolute zero the probability of finding electrons in higher energy levels than the Fermi level is 0.5. In terms of energy levels then any solid may be thought of as a series of energy levels or bands with electrons occupying those up to or below the Fermi level. This knowledge helps in classifying materials according to their electrical usage, as insulator, conductor or semiconductor, and also to explain the production of electrical charge in solid to solid contact charging.

The terms conductor, semiconductor and insulator may be distinguished in three different ways. First, this classification may be made on the basis of resistivity, as illustrated in Fig.2 (from Beck & Ahmed 1973 (6))

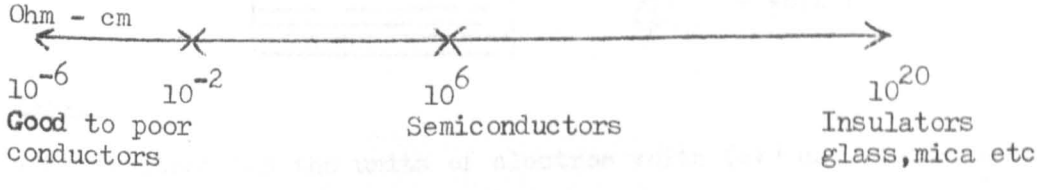


Fig.2 A classification of insulators, semiconductors and conductors according to their approximate resistivity.

Secondly, classification may be made on the basis of the relative positions of the valence and conduction bands. In an insulator the energy band below, but nearest to, the Fermi level (the valence band) is widely separated from the highest band above the Fermi level (the conduction band) and for an electron to leave the valence band and enter the conduction band it would need to acquire a great deal of energy. In the case of semiconductors this band gap is less in width but an electron would still require a considerable amount of energy to leave the valence band, pass above the Fermi level, and enter the conduction band. However in conductors either the gap does not exist and valence and conduction bands overlap, or the valence energy levels are not fully occupied thus allowing migration of electrons with only small additions of energy.

A third way arises as follows :- Consider a substance - in terms of its energy bands: - The Fermi level determines the location of the valence electrons and above this level are unoccupied levels, or bands, into which an electron, given sufficient energy, will move. There is a minimum energy = $\frac{1}{2}$ m v^2 which would enable an electron not only to rise above the Fermi level but also to escape the crystal lattice. This minimum energy is called the work function (ϕ m) (see Fig.3).

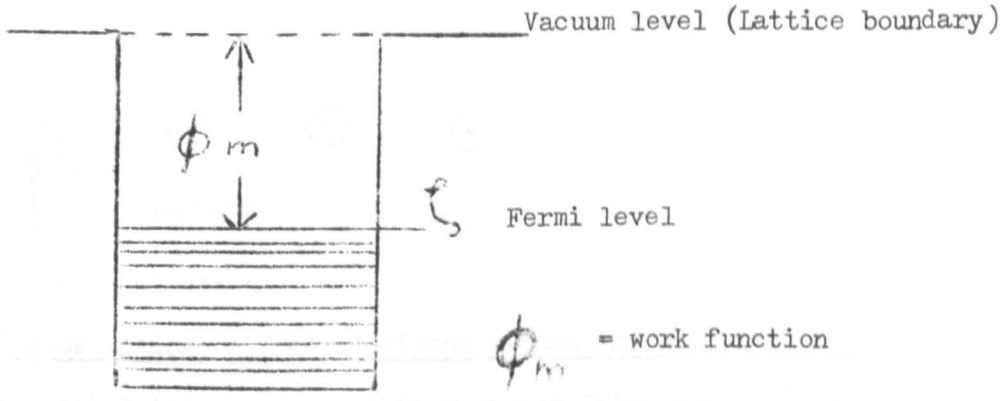


Fig.3

Work function has the units of electron volts (eV) and it is the minimum amount of energy which must be given to the free electrons at the Fermi level to enable them to escape from the crystal lattice. In the case of

metals work functions range from about 1.5 eV to 7 eV.

It follows, from the discussion of band gaps above, that conductors can have low work function values, that is to say that the valence electrons will need less additional energy to escape from the substance; whereas insulators - since they have a wide energy band gap - have high work function values and semiconductors lie in between the two.

To escape from a crystal lattice an electron must acquire sufficient energy to overcome two forces restricting its escape. Within the lattice the electron will experience attractive electrostatic forces from the positive 'fixed' nuclei but the resultant of such forces is zero hence it can move freely within the lattice somewhat as molecules in a gas. However should it reach the ions forming a lattice boundary it will cease to experience symmetric forces and will be, in effect 'suspended' by the forces of the nearest ions, until it tries to pass beyond the boundary when the attractive forces will again come into play - Fig.4.

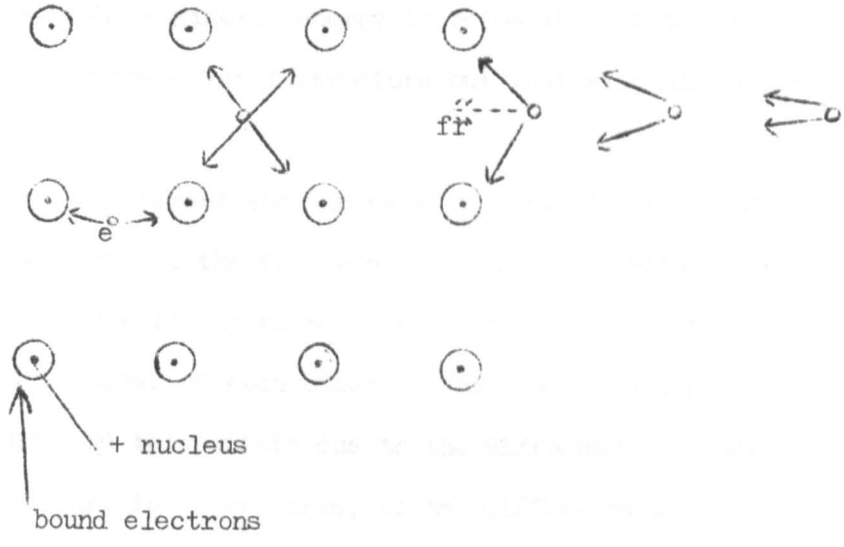


Fig.4 Forces acting on free electrons within and escaping from a crystal lattice. (after Parker,'Electronics'[7])

If the escaping electron has enough energy it will overcome the restraining lattice ion attractive forces but even so it will then experience attractive forces from its own image within the solid, the so called image forces.

Fig. 5 illustrates this situation in which the image force $\epsilon^2 / 4x^2$ (where ϵ = charge on the electron, 1.602×10^{-19}C, x = distance from lattice boundary) acts on an electron escaping from the lattice boundary.

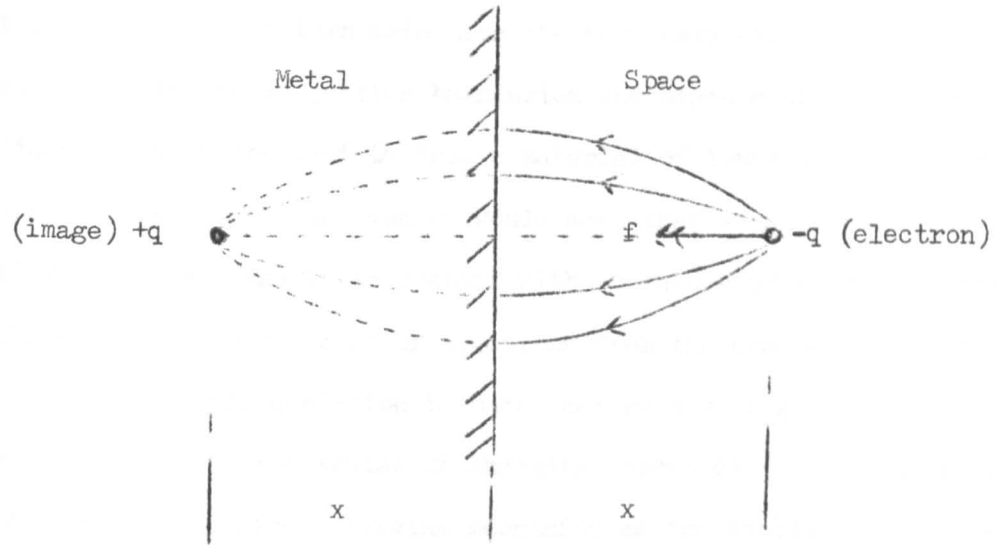


Fig. 5 The electrical image and associate forces on an escaping electron.

The electron whose kinetic energy is below that of the work function will fall back into the crystal structure but that with high enough energy will escape.

If two different substances - for example two metals - are placed in intimate contact, the free electrons drifting within the crystal lattice of each will experience electrostatically attractive forces from the positive nuclei of each other. There will be a potential difference between them and this exists due to the difference in their respective Fermi levels or, in other words, to the difference in their work functions. The electrons of the metal of lower work function will need less energy to escape their lattice boundary and so there will be a movement of electrons from the metal of low work function into the metal of higher work function. This electron movement will reach a dynamic equilibrium, assuming the temperature remains constant, in which the potential difference will have ceased to exist. If the two metals are now

mechanically separated, then that of lower work function will be deficient in electrons and thereby positive in polarity with respect to that of higher work function which, having gained electrons, will be negative.

It would appear that solid - solid contact charging, certainly in the case of conductors, relies on the difference in their work functions which in turn determine the necessary kinetic energy needed by electrons to escape lattice boundaries and migrate across the interface. Since electron movement is from a material of lower work function to one of higher work function it would seem that when a conductor (low work function) is in contact with an insulator (high work function) there would be a movement of electrons from the conductor into the insulator. This condition is under active investigation and some details will be given in the review of charging processes (9.3. 0) using the solid - solid contact charging mechanism as the explanation of the origin of charge.

9.2.1 The Double Layer charging mechanism.

Investigators of the charging processes which occur at a liquid - solid or liquid - gas interface claim that charge is produced by the mechanical shearing of an electrical double layer at the interface. (This discussion omits any consideration of the liquid - liquid interface, say of two immiscible liquids, as it is not immediately relevant to the Leidenfrost charging process).

(i) The double layer at the liquid - gas interface.

Loeb (1956)[2] reviewed the work of Coehn (1898) who had stated, in 'Coehn's Law', that substances with a high dielectric constant in contact with substances of lower dielectric constant charge positively relative to the substance of lower dielectric constant. Coehn's argument was tautological in that the purity of the thirty liquids which he used to obtain his 'law' was determined from their conforming in behaviour to the 'law'. Loeb felt that more investigations were needed before Coehn's Law could be put into proper perspective. At the present

time there does not seem to be any physical reason to expect the behaviour stated in Coehn's Law.

The currently accepted picture of the double layer at the liquid gas interface, used for example by Levin and Hobbs (1971)[8], though specific to the water - air interface, is that first presented by Alty (1929) whose work was reviewed by Loeb[2]. A correlation of Alty's papers, reviewed by Loeb, the outline of his ideas given by J.J. and G.P. Thomson [9](Alty worked in J.J. Thomson's laboratory) and present day ideas of the structure and properties of the water molecule it is possible to arrive at a model of the water - air interfacial double layer. Since the properties and behaviour of water are very important to any consideration of the double layer at the water - air interface it is necessary to consider them in some detail as follows.

A summary of the properties of the water molecule.[10,11,12]

A molecule of water is formed when the two orbitals of two hydrogen atoms overlap the single 2p electron orbitals of an oxygen atom. (The oxygen atom has a filled 1s orbital, a filled 2s orbital, a filled and two single 2p orbitals). The orbital structure of the molecule so formed will enclose the nuclei and have an internuclear, valence bond length, of 0.99 Å. (see Fig.6) (also Appended Material)

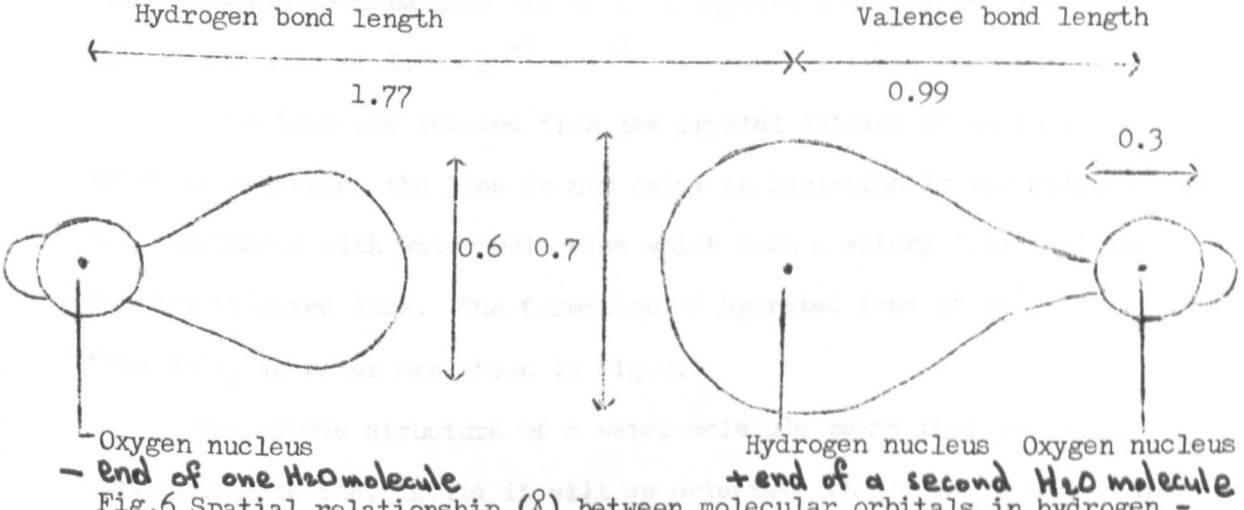


Fig.6 Spatial relationship (Å) between molecular orbitals in hydrogen - bonded water molecules. (from ref. 12)

The eight, electrically positive, protons of the oxygen atom will tend to pull the negative charges of the hydrogen atoms towards them and so make the water molecule into a dipole with the positive bias in the region of the hydrogen nuclei and the negative bias at the filled orbitals of the oxygen atom. (This polar characteristic of water is common to many solvents - see Gurney 1953 [10]). The outcome of this structure is for a water molecule to acquire by electrostatic attraction, hydrogen bonding, four other water molecules to itself to give it a tetrahedral structure. In liquid water, as distinct from ice, this is a short range order since long range order i.e. approximating to a crystalline structure is disrupted by thermal energy.

Even the purest water does not consist solely of H_2O molecules. There is some disociation of molecules and H^+ and OH^- ions are present in equal amounts so that water may be considered, chemically speaking, as an acid or an alkali. The ion concentration is 10^{-7} moles litre^{-1} hence, considering the H^+ ions alone this gives a pH = 7. It is thought that the H^+ ions do not exist in isolation but are attached to water molecules to form hydroxonium ions (OH_3^+) having a mobility of 3.2×10^{-7} m s^{-1} with an applied potential of 10^2 V m^{-1}. Instead of normal ion drift there is a transfer of H^+ ions from molecule to molecule when molecular collision occurs. Hydroxyl (OH^-) ions are thought to behave in a similar manner to hydroxonium ions and with an applied field of 10^2 V m^{-1} they have a mobility of 1.8×10^{-7} m s^{-1}.

When ions are removed from the crystal lattice of an ionic solid by water molecules the ions do not exist in isolation in the solution but are surrounded with water molecules which form a watery 'coating' and so give hydrated ions. The formation of hydrated ions of Na^+ and Cl^- from $NaCl_s$ in water are shown in Fig.7.

The dipole structure of a water molecule means that on its approaching an ionic solid it will so orientate itself as to weaken the internal electrostatic attractive binding forces. Other water molecules

in the region will do the same and the ion will be more attracted to the water molecules than to its neighbours in the lattice and will be detached towards the water molecules having the greater resultant electrostatic attractive force with respect to nearest neighbour ions within the lattice.

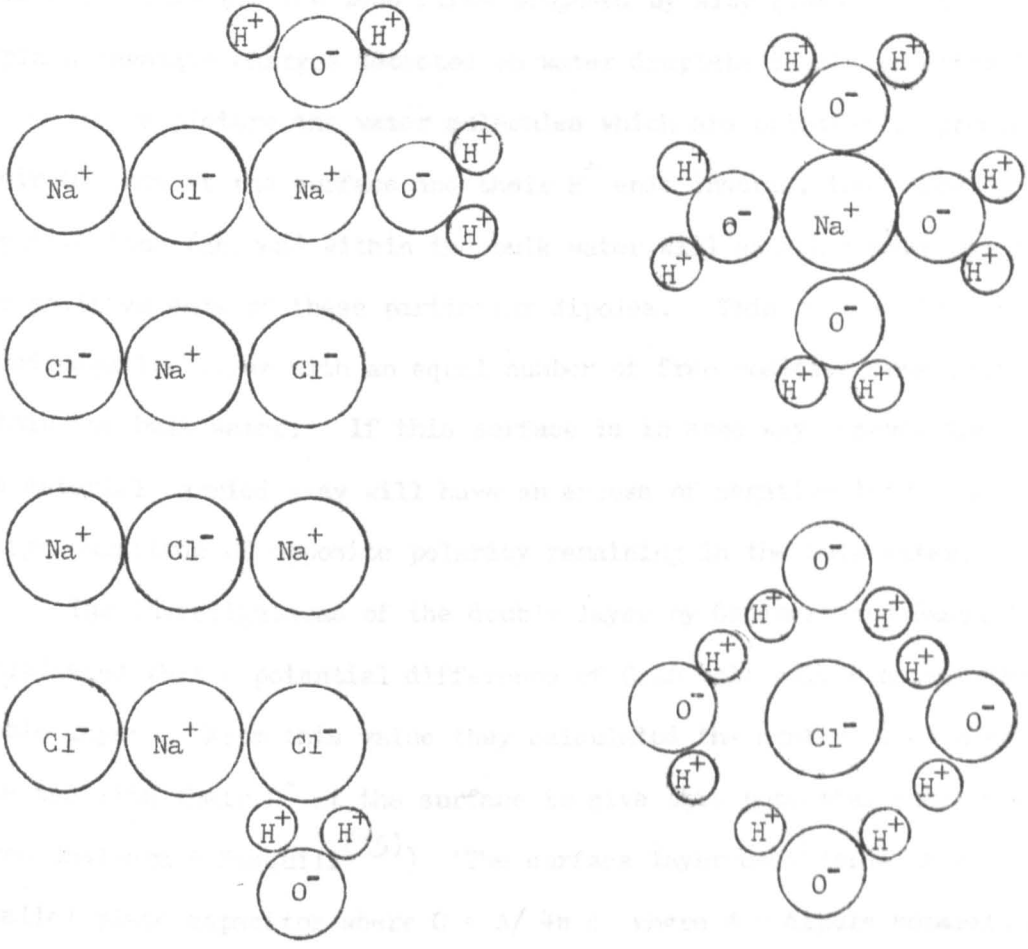


Fig. 7 Left, the removal of Na and Cl ions, from the Na Cl lattice, by water molecules. Right, above, the hydrated Na ion, below, the hydrated Cl ion. (From Bandtock & Hanson [13]).

Where the solid in water is a positive ion lattice with a free electron 'gas' the electrons, on the approach of the negative end of water dipoles will be repelled away from the solid - liquid interface and the same action will occur with positive ions being taken, by electrostatic attractive forces, of water molecules, into solution. (This will be considered in liquid solid double layer discussions to follow).

Liquid - gas double layer

The structure of the water molecule and the electrostatic forces acting between such molecules means that particular molecules tend to be oriented such that the O^- end of the dipole is at the surface i.e. the water - air interface will remain fixed and a negative polarity will be present. This was the idea first proposed by Alty (1929)[14] to explain negative charges detected on water droplets in his investigations.

If we picture the water molecules which are oriented to present their O^- ends at the surface and their H^+ ends inwards, then free negative ions (anions) within the bulk water will attach themselves to the positive ends of these particular dipoles. This results in a tightly bound negative layer with an equal number of free positive ions (cations) within the bulk water. If this surface is in some way removed then the material carried away will have an excess of negative ions, the equal charge magnitude of opposite polarity remaining in the bulk water.

The investigations of the double layer by Chalmers and Pasquill[15] established that a potential difference of 0.26 volt exists across the double layer. From this value they calculated the number of dipoles oriented with their O^- at the surface to give this potential difference viz: (From Chalmers & Pasquill[15]) 'The surface layer considered as a parallel plate capacitor where $C = A/4\pi d$ where d = dipole separation . If σ is charge density in e.s.u cm^{-2} then if A = 1 cm^2 $Q = \sigma$. If $V = Q/C = 4\pi\sigma d$ e.s.u then V, in e.s.u = $0.26/300 = 4\pi\sigma d$, from which σd will be found to be 6.9×10^{-5} e.s.u x cm/cm^2. The H_2O dipole moment = 1.9×10^{-18} e.s.u x cm hence $n\sigma = 3.6 \times 10^{13}$ dipoles cm^{-2} and since a water molecule has an area at the surface of about 9×10^{-16} cm^2 $n_w = 1.1 \times 10^{15}$ (assuming a smooth surface).' Chalmers and Pasquill stated that this indicated that about one in thirty water molecule dipoles are oriented normal to the surface. This is rather difficult to envisage in the light of the structure of water molecules but the idea is still in current use as witness Levin & Hobbs (1971)[8] (9.4.4).

The double layer at the liquid - solid interface.

The model of the double layer at the liquid - solid interface is subject to modification as time goes on because of ongoing research in several branches of physics and chemistry (in particular in electrochemistry, physical chemistry of surfaces, surface physics and electrostatics). The view now to be presented is a correlation of material from Gurney (1953)[10], Adamson (1967)[16], Faust & Hunter(1967)[17], Adams (1968)[18], Parsons(1971)[19], Rao (1972)[20], Moore (1974)[11], and Ottewill (1975)[21].

The history of the liquid - solid double layer dates from Helmholtz (1879). His original hypothesis of ions tightly bound to a metal surface was modified by Gouy (1910) and Chapman (1913) and the Gouy - Chapman model was in turn modified by Stern (1924). The current model is the Stern double layer explained in the light of modern ideas on the behaviour of ions in solution and the atomic structure of solids. (Although we talk of the liquid - solid interfacial double layer the solids most studied have been metals, and the liquids have been electrolytes simply because these have found the most practical application in cells and batteries of cells).

In a metal there is a lattice of positive ions between which electrostatic repulsion, trying to drive the ions apart, is reduced by the presence of free mobile electrons. An electrolyte has no free electrons, only ions, and if it is an aqueous solution the ions will be hydrated. There is a difference in energy levels between the solution and the solid in that the energy level of the solution is higher. This being the case it has been found that the positive ions of metals go into solution. Consider for a moment the energy required to take out a positive lattice ion into a vacuum: once out of the lattice the ion will experience its electrical image force attracting it back into the lattice. The image force is present due to the excess of free electrons, in the metal, and energy is therefore needed to remove the ion away

from the surface against the attractive electrostatic force. The image force is to some extent counteracted by ions which are mobile in the electrolyte and which are themselves attracted to the metal surface. Also as the former lattice ion enters the electrolyte the dipolar water molecules will be attracted to it and so it will become hydrated. Positive ions will continue to leave the metal lattice until the increasingly negative metal surface makes escape more and more difficult until finally an equilibrium condition prevails in which the metal surface is negative, due to its free electrons, unable themselves to escape into the solution due to positive lattice ion attractive forces. Thus the metal surface is negative and in the solution, at the interface, positive ions from the solution attach themselves, by electrostatic attraction to the metal. This constitutes an electrical double layer. However this simple picture is not accurate as no consideration has yet been given to the attraction of negative electrolytic ions to the deposited positive layer, or to the more massive hydrated ions. An illustration of the real situation is shown in Fig. 8 (from Adamson).

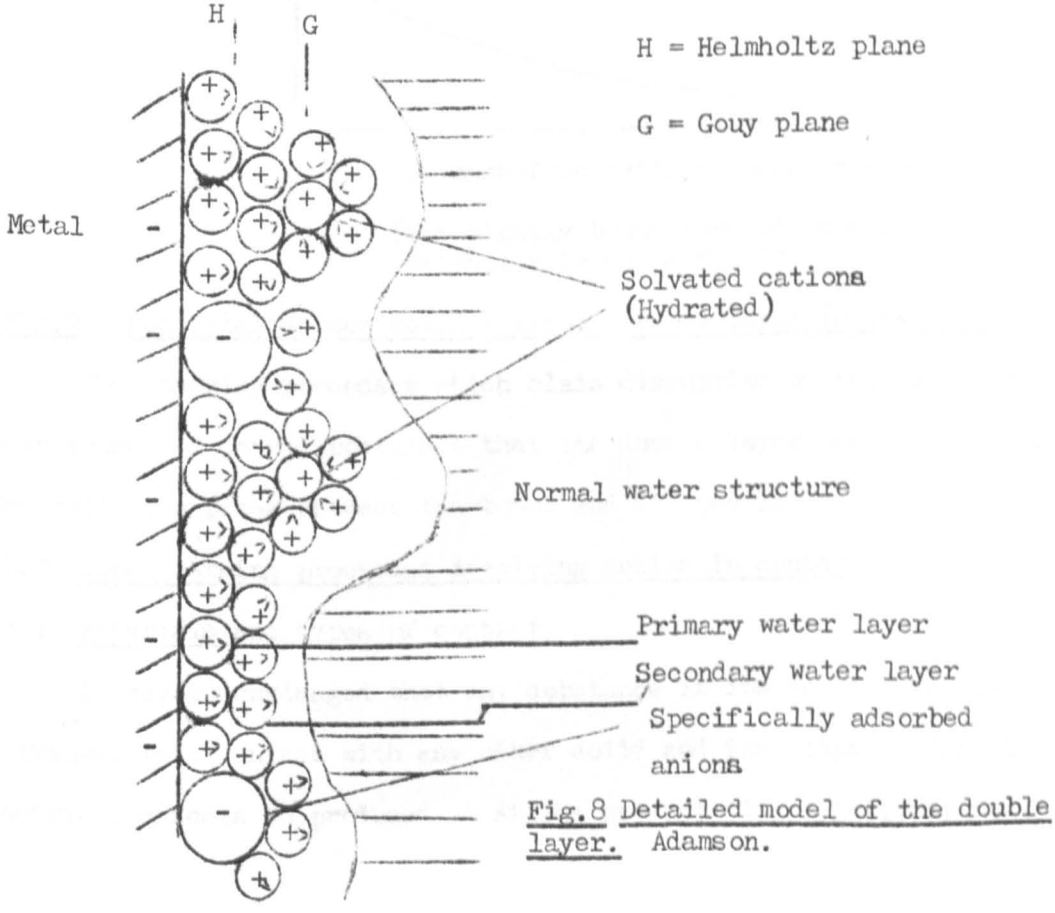


Fig.8 Detailed model of the double layer. Adamson.

The double layer is now thought to consist of layers of ions in various planes with the bonding, i.e. electrostatic attractive forces, becoming weaker away from the metal surface. In consequence of this there exists at the farthest 'electrolyte/liquid' boundary a weak diffuse layer subject to disruption by thermal energy greater than electrostatic attraction. The potential difference across the double layer was proposed by Ottewill[21] to be as shown in Fig. 9 in which there is a linear fall across the phase boundary of solid to tightly bound electrolytic ions and an exponential through the more diffuse ion layers into the electrolyte.

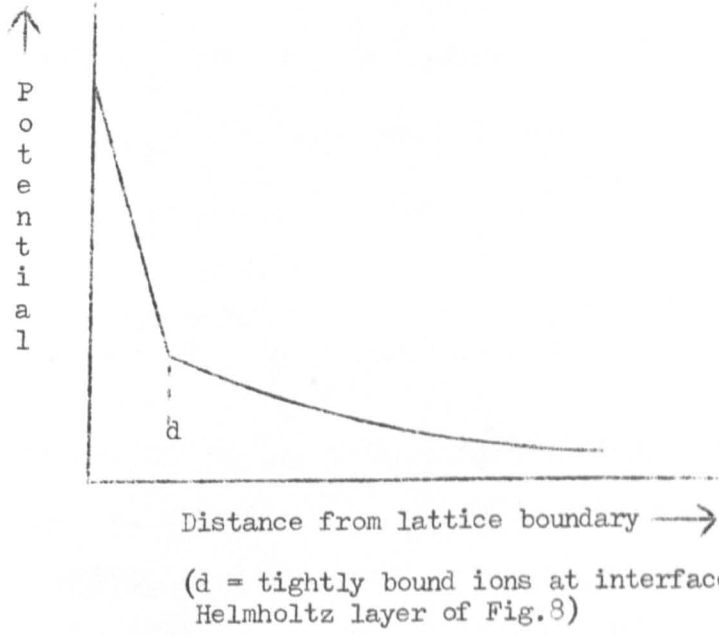


Fig.9 Potential across solid - liquid double layer (Ottewill).

The charging processes which claim disruption of this layer as their source of charge postulate that the double layer may be mechanically 'sheared' at a plane between the bound and diffuse layers.

9.3.0 Some charging processes involving solids in contact.

9.3.1 Materials and types of contact.

It may be envisaged that any substance in its solid form could be brought into contact with any other solid and investigated for the electrical effects so produced. At the present time relatively few

substances have been involved in such investigations and the choice has been made either on the grounds of their use in industrial manufacturing such as plastics and textiles, or in natural phenomena where dusts or ice are in evidence.

Solids may come into contact by impact which may cause plastic or permanent deformation in the region under the point of impact. They may slide and, depending on force, ploughing or shearing away of material may occur. Also substances may roll across each other.

The area in contact between two solids depends on the applied force, surface structure and hardness of the material. Table 1 (from Bowden & Tabor 1956 [22]) gives the area of contact between flat steel surfaces:-

Load in Newtons	True area of contact in cm^2	Fraction of macroscopic area in contact
5000	0.05	1/400
1000	0.01	1/2000
50	0.0005	1/40 000
20	0.0002	1/100 000

Table 1

The word 'flat' is a relative term since a surface which, after meticulous grinding and polishing, may look flat to the unaided eye will be found on microscopic examination to have projections. Fig.10 illustrates two such surfaces (from Bowden & Tabor 1956)

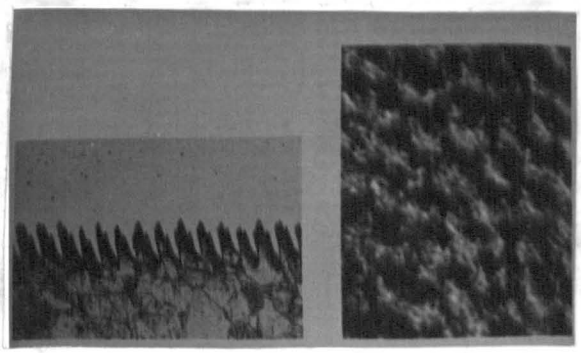


Fig.10 Left: Finely turned copper surface, projections about 5×10^{-6} m high; Right: Electron micrograph of an electrolytically polished aluminium surface with projections between 10^{-7} & 10^{-8} m high.

The contact of two surfaces is between microscopic projections which bear the applied force, the resulting pressure from which may cause melting and thereby microwelding. In separating the two surfaces these microwelded regions will be torn so that pieces of one material will be transferred to the other. Autoradiographic methods, in which one material - usually the softer - is radioactively labelled show that even the most delicate contacts of surfaces remove pieces of the softer material. The problem of oxides on surfaces may be removed by preparing and contacting the surfaces in vacua.

Adam (1968)[23] has reported that the polishing of a metal surface changes the surface to that of an amorphous assembly of atoms which electron diffraction methods indicate to be more like a liquid or glass than the more familiar crystalline structure of a metallic solid. Furthermore that the atoms in this polished surface, from the diffuse rings of the electron diffraction technique, appear to occupy less than their normal volume as if the outer electrons have in some way been rearranged. The estimated depth of this amorphous layer is stated to be about 30Å. The properties of this layer are different from those of the bulk solid in that the layer is much harder and more soluble and electrolytically more anodic such that corrosion is always first apparent on a polished surface or where polishing has occured say due to punching a hole through the solid. In addition this amorphous surface layer seems able to dissolve other metals - something which the crystalline bulk material cannot do - and it has been found that metals deposited from their vapours on to this layer first give the pattern peculiar to their crystalline structure but within seconds this disappears. (Adam gives an example in which zinc on polished copper would not give the diffraction pattern for zinc until 'very many successive depositions'). The heat of solution of these surface layers has been found to be higher than that of the crystalline solid and it is suggested, by Adam, that some of the mechanical energy of rubbing and polishing is stored in them.

These factors must be taken into account in any solid - solid contact experiments designed to investigate the charge produced and thereby determine the charging mechanism.

9.3.2 Investigations of Gander and Latham.

Gander and Latham[24] devised an apparatus in which they could control contact time, impact and separation velocities, temperature and obtain non - frictional contacts. They investigated charging which occurred when brass was brought into contact either with rubber or ice and decided that final values of charge on surfaces were discharge limited due to the surrounding air.

9.3.3 Investigations of Davies.

Using a similar apparatus to that devised by Gander and Latham, Davies (1969)[25] measured charge densities on dielectrics due to controlled contacts with metals, of known work function. His results are given in summary below:- (quoted from ref 25)

(i) The charge generated on dielectric surfaces by metallic contact in vacuo is dependant on their work functions.

(ii) Dielectric work functions may be determined by the measurement of the contact charge generated by metals of known work function; (P.V.C. 4.85 eV, Polymide 4.36 eV, P.T.F.E. 4.26 eV, Polycarbonate 4.26 eV, P.E.T. 4.25 eV, Polystyrene 4.22 eV, Nylon 66 4.08 eV.)

(iii) The present data form a basis for describing the complex charging phenomena that occur under practical ambient conditions.

(iv) The establishment of the concept of work function, and more generally electron energy levels, in insulating polymers is widely significant. The characterisation of polymers in terms of electron energy levels and the understanding of charge injection mechanisms contribute significantly to the elucidation of conduction and dielectric loss processes in these materials.

9.3.4 Investigations of Bauser, Klöpffer & Rabenhorst.

Some support for Davies' statements came from Bauser, Klöpffer

and Rabenhorst (1971)[26] who investigated charges produced by metal to insulator contact. They stated that electron transfer was the charging mechanism. This electron transfer, leading to the establishment of charged surfaces, had a linear relationship to the work function of the materials used.

9.3.5 Investigation of O'Neill & Foord.

The investigation of polymer surface charging carried out by O'Neill and Foord (1975)[27] demonstrated the importance of work function and also emphasised the difficulty of achieving reproducibility due to high resistivity of materials and the importance of surface preparation.

9.3.6 Investigations of Lowell.

Recent publications by Lowell (1976,1977)[28,29] include evidence that a single metal - polymer contact produces charge not dependant on the metal workfunction but that repeated contact or sliding supports the idea that the final, or surface saturation,charge on a polymer depends on metal work function. Material transfer may play some part in charging but this is not the primary reason for charge generation.

9.3.7 Investigations of Robins, Rose - Innes & Lowell; Baum & Lewis.

The earlier paper by Robins, Rose - Innes and Lowell (1975)[30] described an investigation of cooled polarised pyroelectrics sprayed with ions of specific polarities prior to their contact with a metal surface. They felt that neutralisation of insulator surface ions affected the surface charging of insulators. Baum and Lewis (1975)[31] deposited ions, of a chosen polarity, from a Nernst filament on to insulator surfaces and found that these ions would remain stable for long periods. At a surface temperature of 100°C to 150°C surface ions were neutralised, it was suggested by carriers from within the bulk material.

9.3.8 Investigations of Norhage and Bäckström; Das Gupta & Noon.

Norhage and Bäckström (1975)[32] concluded , from an investigation of contact between polymers and metals, that the charged layer on polythene had a thickness of 40nm to 100nm. Using x - ray diffraction, optical

observation with coherent light and infra red resonance spectra techniques Das Gupta and Noon (1975)[33] searched for changes in the structure of polythene and for the presence of micelles (embryo crystals) when the material was subject to electrical stress. They decided that charge moves or hops along a system of micelles, presumably under the applied electrical stress, until reaching a defect which presents a barrier to further conduction and so a site of charge is produced. By examining changes in these defect 'barrier' charge zones, due to the presence of an electric field it was found that defect density increased by about 12% in a field of 3×10^7 V m^{-1}. They planned further work on the 'crystallinity' of polymers the results of which will probably help to resolve the question of charge transfer in polymers as well as provide knowledge of the structure of polymer insulators.

9.3.9 Dust Clouds.

It is well known that two disimilar materials when rubbed together i.e. brought into contact will produce charge. It is less well known that two identical pieces of one material will produce charges of opposite polarity when the rubbing of one on the other is asymmetrical. This was discovered by Bergman (1765) and partly investigated by Rudge (1914)[34] whose work was followed up in a series of publications by Shaw and Jex (1926)[35] and Shaw (1926-7)[36,37]. Shaw (1928)[38] extended his study of asymmetrical charging to try to explain the charge produced in dust clouds. Also in 1928 Blacktin[39] investigated charging in coal dust clouds and found that charge increased with particle size, the speed of the transporting air current and the amount of dust. Kunkel and Hansen (1950)[40] measured the charge on particles of quartz - using a dark field ultramicroscope. They stated that charge appeared on initial particle separation into a cloud and was not due to impacts between particles in the cloud.

The dust storms which occur in India and in Death Valley U.S.A., were studied by Kamra (1971)[41,42]. He found that clay minerals always

produced net negatively charged clouds whereas gypsum clouds may be of either polarity. (Kamra gave no explanation for this but clays are usually aluminium silicates - and contaminated with various impurities - gypsum $Ca\ SO_4\ 2\ H_2\ O$ tends to be found in bands and, in its natural locations would be expected to be more 'pure' that is less contaminated than clays. This being the case it is difficult to see why the clays produced consistent net negative polarity and gypsum did not.)

Many industrial situations involve the transport of powders through pipes, for example flour, metal powders and drying agents. Ramackers (1970)[43] investigated charging when silica particles of mean diameter 64 μm were transported, by air, through metal pipes. He measured the current to earth from the pipe when various quantities were transported at various air speeds through it and proposed an empirical equation for space charge density (Q_s) which, for reasons not given, takes no account of the kind of metal used!

$$Q_s = 10.4\,\rho^{0.73}\,v^{1.15}$$

where $Q_s = \mu C\ m^{-3}$

ρ = solid 'load' $kg\ m^{-3}$

v = gas velocity ms^{-1}

Obviously from a practical standpoint such empirical studies of particulate cloud charging are important but the solution of how the solid - solid contact charging mechanism operates for particular processes will have to come from refined laboratory investigations which take into account the properties and preparation of surfaces, their behaviour on contact and the means whereby there comes about a redistribution of the electrons of the materials involved.

Some indication of the state of play, as it were, of such investigations into solid - solid contact charging may be gained from a recent literature survey by Gallo (1977)[44].

9.4.0 Some charging processes involving the double layer charging mechanism.

9.4.1 Waterfall, Spray electrification and space satellite engines.

Elster and Geitel (1890) had found that the fine spray near waterfalls carried a negative charge with a positive charge on larger water drops. Lenard investigated this phenomenon - which he called, 'Waterfall electricity' - by the use of air blasts to break up water into droplets ranging in diameter from 0.17 mm to 0.00067 mm. Pure water from an atomizer produced 7×10^{-7} C kg^{-1} as a negative spray with an opposite charge on large drops or on the atomizer.

Coehn and Mozer (1898) with Lenard felt that charge was produced by a shearing of the double layer at the air water interface - strictly speaking at the boundary of the bound and diffuse layers in the water. Spray electrification was mainly associated with natural phenomena until the advent of the super tanker, several of which were seriously damaged by explosions during cleaning. Lawes[45] discussed this in the light of spray electrification from high pressure water jets used in tank washing.

Gibson (1975)[46] reviewed aspects of spray charging investigations of recent times noting that charge densities of 10^{-3} to 10^{-5} C m^{-3} are produced in clouds of sprayed liquids. Spray electrification can be put to use. The spraying of liquid paints in the form of charged droplets is much used with the paint being charged from a corona source or similar device incorporated in the spray gun.

Perhaps the most fascinating use of deliberately induced spray electrification is in satellite engines of the so called colloid type. Lines, Makin and Bright[47] published details of the use of electrically atomised liquids from needle jets to power thruster engines used in the orientation of satellites.

9.4.2 Bursting bubble charging.

The total area of the oceans and seas is about 3.6×10^{8} km^{2}.

Blanchard[48,49,50] estimated that some 0.8 $\mu g\ s^{-1}\ m^{-2}$ of salt is produced in the form of 'small raisin shaped irregular globs' to a total of 9×10^9 metric tons annually. Blanchard found that these salt nuclei are produced in droplets flung upwards by bursting bubbles in seawater. They are positively charged with an average charge of 2×10^{-17}C and, in Blanchard's experiments, were produced by bubbles ranging in diameter from 0.04 mm to 1.7 mm which produced droplets ranging from 3.8 μm to 174 μm diameter. These droplets evaporated to leave salt nuclei weighing from 1×10^{-12}g to 1×10^{-7}g. In conjunction with Woodcock(1953) Blanchard[51] published details of a film of bursting bubbles taken at 3,000 frames s^{-1}. It was found that droplets from 1 μm to 20 μm came from the breaking up of the bubble film and the jet produced by the collapsing bubble cavity.

9.4.3 A recent study of ultrasonic atomisation.

Using an ultrasonic transducer to manufacture a liquid fountain Bassett[52,53] produced charged droplets which were found to have an approximately Gaussian charge distribution with a maximum value of 5×10^{-17}C (500 electrons) on droplets of diameters ranging from 1 μm to 20 μm, with a peak in the size distribution at 9 μm. The production of the droplets was studied by an ultra high speed filming technique[54] which showed that droplets came from an oscillating surface in a column of bubbles at the apex of the ultrasonically induced fountain. Despite a very short delay of only 8×10^{-7}s between frames, the actual mechanism producing the droplets was not apparent.

9.4.4 Charge from Splashing.

Lenard[55] had noted that charge was produced when water impacted on a solid surface. The study of this by Levin and Hobbs(1971)[56] proved that charged droplets are produced by water and dilute aqueous solutions splashing on dry and wetted solid surfaces. They found that positive charge of the order of 10^{-15}C was left on a surface after splashing, an equal and opposite polarity of charge was assumed to be

carried on droplets of 10 μm radius produced from jets on the crown of the splashing drop.

9.5.0 Some examples of charging processes to which no particular mechanism has yet been generally agreed.

9.5.1 The school laboratory introduction to electrostatics.

All early investigations of electrostatics obtained electricity by rubbing a rod or tube with some kind of fabric (Stephen Gray for example used a glass tube about a yard long rubbed with silk[57]). Primary school children rub their plastic (PVC) pens on their nylon jumpers and senior school children witness the more serious demonstration of the Science Master rubbing a glass rod with silk and an ebonite rod with fur. As yet there is no agreed explanation of how this simply demonstrated charging process works. Is it that electrons transfer in an adjustment of Fermi levels due to the different work functions of the materials? Or is it, as those claim who disagree with the solid - solid contact mechanism in this case, due to a shearing of the double layer of water or fatty acids at the interface of the two rubbing materials?

9.5.2 Charging by freezing.

Workman and Reynolds in 1950 found that as ice froze out of weak, aqueous, electrolytes (10^{-3} to 10^{-6}M), large potentials could be measured between the liquid and the ice (in the case of NH_4 OH this was 230 V). The water was found to be negative and some suggestion was made that preferential migration of ions took place into the ice at the phase change.

This discovery has implication in atmospheric electricity and Mason[58,59] has shown that a water droplet, in freezing, becomes contained within an ice shell which fractures and emits the liquid contents to form ice splinters. The freezing would produce charge as would the contact between colliding ice splinters as well as water splashing on frozen surfaces (see Levin & Hobbs). The slow freezing of a water droplet produces an ice shell from which a spicule grows (Blanchard[60]). (Mason

obtained photographs of this.)

Much investigation of charging during freezing is in progress in addition to the process of freezing itself (Mason[61], also Chisnell & Latham[62]). The importance of the freezing charging process for thunderstorm electrification is hotly debated at the present time (Mason & Moore [63,64]).

9.6.0 Concluding remarks.

'This is not the end. It is not even the beginning of the end,
But it is, perhaps, the end of the beginning.'

W.S. Churchill, 1942.

Most of the work described in this chapter has taken place in the twenty or so years since Loeb and Harper made their pessimistic remarks cited in the introduction. It is apparent that the situation has improved in that many processes have been identified and the charging mechanisms are becoming more clearly understood. It would be unwise to try and predict a final set of answers and classifications since, as with most scientific research, a question answered is accompanied by more questions asked.

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10.0.0 Energy conversion in particle emitting Leidenfrost drops and some speculations on contributory charging mechanisms to the charging process.

10.1.0 Introduction.

The Leidenfrost boiling of an aqueous solution drop with its attendant particle emission involves energy in diverse forms. Attempts will be made in this chapter to identify these forms of energy, estimate the magnitude of particular forms and also obtain empirical equations relevant to the Leidenfrost drop situation.

In the preceding chapter a distinction was made between the terms charging mechanism and charging process and it was suggested,and for some examples shown, that processes may be collected into sets and a particular mechanism assigned to each set. An attempt will now be made to assign the most likely charging mechanism or mechanisms to the process which in the present work has been discovered to produce charged particles when an aqueous solution undergoes Leidenfrost boiling. The first part of the speculation will be qualitative leading to a comparison of data.

At the moment theoretical predictions for different processes are not specific enough to allow clear experimental identification of mechanisms operating. In addition there is inadequate data, and no conclusions have been reached on explanations of the basic charging mechanisms, which are subject to ongoing investigations. I cannot therefore claim that my attempts, in the following sections, to single out the most important mechanisms operating in my own experiments are any more than tentative suggestions.

Having set out the measurements on radius, evaporation time etc., we are now finally in a position to put them all together to make up a list of energy exchanges taking place during particle emission. (Note that this is not an energy budget over the whole lifetime of the drop).

10.2.0 On the forms of energy.

Consider again an aqueous solution drop undergoing Leidenfrost boiling: It hovers above the heated surface on a layer of its own vapour and water is evaporated thereby leading to solute concentration and precipitation. A precipitated crystalline skin forms on the underside and the vapour support is shut off causing the drop to fall and the crystalline material to touch the hot surface. This material along with some of the concentrated drop solution is 'explosively' ejected laterally from beneath the drop in what is termed particle emission. The material ejected forms electrically charged solute particles from already precipitating solution. After particle emission the steady condition of the drop is restored until the next particle emission.

We may consider that the drop has a condition in which steady energy conversion is taking place in that heat enters the drop to bring about the phase change liquid to gaseous water. Also salt is precipitating and adding to this heat - since the formation of $Na\ Cl_s$ is an exothermic reaction. The drop has a condition of rapid energy conversion during the particle emission period in which the potential energy of position becomes kinetic as the drop falls,* there is heat transfer across the $Na\ Cl_s$ crystalline skin, electrical energy, evaporation - evolution of steam, surface tension energy due to work being done in breaking up a portion of the drop and forming many small droplets and also kinetic energy in ejecting the droplets away from the heated surface.

We may summarise the input and output energy of the drop during particle emission thus :-

Input energy = Heat(conduction) + Radiation

Output energy = Kinetic + Electrical + Surface Tension + Heat(evaporation & precipitation) + Radiation

*This particular energy conversion is negligible and is not further discussed.

In order to calculate the heat needed to evaporate water, and the heat gained from salt precipitation, we must perform the following calculation.

Heat energy input needed for phase change liquid to gas $= m \times L$ J where m = mass of drop gm

L = latent heat vap.

$= 2256 \text{ J gm}^{-1}$

(Drops used in the investigation were of 1 ml 3.5% $NaCl_{aq}$)

Phase change heat energy $= 1 \times 2256$ J

$= 2256$ J

Heat contributed by exothermic reaction $NaCl_s$ precipitation = 898 cal mole^{-1} in 1 litre of water (from Kaufmann (1)) which in other words means that 58 gm $NaCl_s$ in 1,000 gm H_2O gives off $898 \times 4.18 = 3753$ J.
In the case of a particle emitting Leidenfrost drop the solution is 6M and would therefore involve $6 \times 3753 = 22518$ J litre^{-1}. A 1ml drop would therefore involve $\frac{22518}{1000} = 22$ J.

Amount of heat energy consumed by a 1ml drop by evaporation or precipitation over its 130s evaporation period = 2256 - 22 J

$= \underline{2234 \text{ J}}$

Rate of heat intake $= \frac{2234}{130} \text{ Js}^{-1}$ (W)

$= 17.18$ W

(This figure will be used under "evaporation energy during a particle emission.")

Energy involved in a single emission of particles.

When the crystalline skin touches the hot surface heat travels through the salt 'bridge'.

Heat flow through salt bridge $Q = \frac{k A (\Theta_2 - \Theta_1)}{l}$ W ($J s^{-1}$)

where k = thermal conductivity of NaCl
$= 0.00092 \text{ Wm}^{-1} \text{ K}^{-1}$
l = length of salt bridge
A = area of contact

$\frac{(\Theta_2 - \Theta_1)}{l}$ = temp. gradient

Assume area (A)contacting hot surface = 10^{-3}mm^2 (10^{-5}cm^2)

then, asssuming l = 10^{-3}cm

$$Q = \frac{(9.2 \times 10^{-2}) \times (10^{-5}) \times (5 \times 10^{2})}{10^{-3}}$$

$$= 4.6 \times 10^{-1} \text{ J s}^{-1}$$

Assume a contact time (i.e. particle emission time) = 10^{-2} s

then energy transferred = $4.6 \times 10^{-1} \times 10^{-2}$ J

$$= 4.6 \times 10^{-3} \text{ J}$$

This value is questionable in that it (i.e. 4.6×10^{-1}J s^{-1}) equals power of 0.5 Watt which when considered for the total area of the hot surface plate of area 100 cm^2 approx would require some 10^7 W ! The duration of contact is a reasonable assumption, it is taken from chart values of pulses, and the area of contact seems reasonable hence the assumed length of the salt bridge must be queried. If it is assumed that the length of the bridge (l) is about 1 mm then:

Energy transferred by heat flow across the salt bridge

$$= 4.6 \times 10^{-5} \text{ J}$$

Examination of photographs of particle emission indicate that about a quarter of the drop is involved in particle emission by being broken up. If the volume of the drop is 1 ml then 0.25 ml will be involved in particle emission.

Surface tension energy.

Area of 0.25 ml drop = 1.92×10^{-4} m^2

No. of 10μ m radius droplets in 0.25 ml

$$= \frac{0.25 \times 10^{-6} \text{ m}^3}{4/3\ \pi\ (10^{-5})^2}$$

$$= 5.97 \times 10^{7}$$

Total area of 10μ m droplets $= 4\ \pi\ (10^{-5})^2 \times 5.97 \times 10^{7}$

$$= 7.50 \times 10^{-2} \text{ m}^2$$

The work done against surface tension ($0.073\ Nm^{-1}$) in changing the 0.25 ml drop into approximately 60×10^6 droplets each of 10μ m radius would be

$$= 0.073\ (7.50 \times 10^{-2} - 1.92 \times 10^{-4})\ J$$

$$= 5.46 \times 10^{-3}\ J$$

In one particle emission an average 500 particles are emitted so the

Surface tension energy involved in a particle emission

$$= \frac{5.46 \times 10^{-3}}{5.97 \times 10^{7}} \times 500\ J$$

$$= 4.6 \times 10^{-8} J$$

Evaporation energy during a particle emission

when 0.75 ml is evaporated by energy $= 2234 \times 0.75\ J$

$$= 1675\ J$$

In each emission evaporation energy $= 1675 \times \frac{500}{5.97 \times 10^{7}}\ J$

$$= 1.40 \times 10^{-2}\ J$$

Radiation energy to drop per emission (by Stefan's Law)*

$= 5.67 \times 10^{-8}\ Wm^{-2}K^{-4} \times 2 \times 10^{-4} \times (873^4 - 373^4)$

(Stefan's constant) (Drop base area) (balance of emission & absorption)

$$= 6.36\ W$$

During time of an emission radiation energy

$$= 130\ s \times \frac{500}{5.97 \times 10^{7}} \times 6.36\ J$$

$$= 6.93 \times 10^{-3}\ J$$

Kinetic energy of an emitted droplet

$$K.E = \frac{1}{2} m v^2\ J$$

Assume droplet density is that of water

$D = 10^3\ kg\ m^{-3}$

$$\text{Mass } m = \text{Volume } V \times \text{Density } D$$

$$\text{then } K.E. = \frac{1}{2} V D v^2$$

The velocity component (v) was estimated from tracks of ejected droplets photographed in stroboscopic light and on average was equal to $6\ m\ s^{-1}$.

---

*This does not include the much smaller term, depending on $(373^4 - 293^4)$, resulting from radiation exchange between the top of the drop and its surroundings (at about 293K (20°C).

The K.E. of a droplet of 10μ m radius $= \frac{1}{2} \times 4/3\pi \times 10^{3} \times 10^{-18} \times 10^{3} \times 36$ J

$= 7.56 \times 10^{-11}$ J

The total kinetic energy per emission of 500 droplets

$= 7.56 \times 10^{-11} \times 5 \times 10^{2}$ J

$= 3.78 \times 10^{-8}$ J

Electrical energy per particle emission

$$E = \int VI \, dt \quad J$$

To obtain values of voltage (V) a quadrant electrometer (Modern Kelvin type, Walden Precision Instruments Ltd.) was set up in hetrostatic mode. (A quadrant electrometer directly connected is said to be in the idiostatic mode in which case the scale is non-linear and needs about 70 V for F.S.D. In the hetrostatic mode a dry battery is connected across one pair of quadrants. A linear scale reading is obtained and sensitivity is about 4 V for F.S.D., this being determined by the dry battery potential). The electrometer was connected across a drop, by an immersed probe, and the metal hot surface. On particle emission voltages of 0.6V to 1.2 V were measured.

To obtain values of current (I) - although a chart record had been made this was found on examination to show few distinct peaks - values from the charge/decay curve for a particle emission were plotted on log-lin paper. A straight line was obtained indicating that charge per emission (Q) was related to other factors by a law of the form $Q = a\, e^{bt}$.

$\log Q = \log a + B\, t$ where $B = b \log e$

t	2s	3s	
Q	2.24	1.08	($\times 10^{-10}$C)
log Q	0.3502	0.0334	

$0.3502 = \log a + 2B$ -----(1)

$0.0334 = \log a + 3B$ -----(2)

$0.3168 = / - B$

$b \log e = -0.3168$

$$b = -\frac{0.3168}{\log e}$$

$$= -0.7294 \quad (-0.73)$$

Subs in (1) $0.3502 = \log a + 2x - 0.3168$

$$\log a = 0.9838$$

$$a = 9.634$$

Therefore $$Q = 9.634\, e^{-0.73t} \ (\times 10^{-10})\ C \quad ---(3)$$

The rate of decay of charge $\frac{dQ}{dt} = -7.03\, e^{-0.73t}\ C\ s^{-1}$

Since current (I) amps is a movement of charge with time viz. $C\ s^{-1}$

then $$I = -7.03\, e^{-0.73t} \ (\times 10^{-10})\ A \quad ---(4)$$

Values of t, from a chart record of pulses produced by each particle emission, were put into (4) and the values of (I) thereby obtained used with measured values of (V) to give:-

Electrical energy involved in a particle emission = 2.7×10^{-10} J

Energy involved per emission of 500 particles (10μm radius)

Heat input energy = (4.6×10^{-5} → 4.6×10^{-3} J via NaCl bridge) + (6.9×10^{-3} J) by radiation

Surface tension	Evaporation	Kinetic	Electrical
4.6×10^{-8} J	1.40×10^{-2} J	3.78×10^{-8} J	2.7×10^{-10} J

A check on vapour layer thickness.

The measurement of voltage on particle emission makes possible a check on the values of vapour layer thickness first determined by photography in 5.1.2 and later by charge magnitude and pulse rise time in 7.2.3.

If, as in 7.2.3, the drop, vapour layer and hot surface are regarded as a parallel plate capacitor in which capacity $C = \frac{Q}{V}$

then, since $\frac{Q}{V} = \frac{\epsilon A}{h}$

$$\text{Vapour layer thickness } h = \frac{\epsilon V A}{Q} \text{ m} \quad \text{----(5)}$$

Area of drop base (A) = 190×10^{-6} m^2

Q per particle emission = 10^{-10} C

$\epsilon_0 = 8.85 \times 10^{-12}$ F m^{-1}

$\epsilon_r = 1.0039$ (permittivity of vapour in layer)

Values of vapour layer thickness (h) obtained from (5) for

V = 0.6 V, h = 0.009 mm; V = 1.2 V, h = 0.02 mm .

These values are of the same order of magnitude as the 0.06 mm obtained in 5.1.2 & 7.2.3 thereby making other calculations involving vapour layer thickness of reasonable validity.

10.3.0 Speculations on mechanisms contributing to the Leidenfrost charging process.

10.3.1 Qualitative speculations.

Consider the sequence of events after the crystalline skin of solid Na Cl has formed on the underside of a saline drop and shut off the supporting vapour layer :-

(i) The Na Cl_s makes contact with the solid material of the heated surface. This constitutes a situation of solid - solid contact charging similar to that studied in the experiments of Latham, Davies, O'Neill & Foord and Lowell (see review in chapter 9) and is one source of charge.

(ii) The decrepitation of crystalline material results in charged fragments (see chapter 8) and the breaking apart of the crystalline skin is likely to produce charge.

(iii) The 'explosion', by decrepitation, of the crystalline material will cause a sliding contact between solid salt and the hot surface material. This sliding of solids in contact can cause triboelectrification (frictional charging). (It is also possible that softer material may be removed by the harder (see chapter 9).

(iv) The 'explosion' also breaks up part of the drop surface and pieces of the drop are flung clear in droplet form - the progenitors of particles. This could mean that the surface double layer is sheared. (This usually occurs where bubbles are in evidence which they are not in Leidenfrost drops. In the case of flash boiling of saline solution there is frothing and considerable bubble production.)

(v) Also during this explosive phase the solution, which is an electrolyte, must touch the hot surface prior to a new vapour layer being established to support the drop. (This was confirmed by chart records of vapour layer resistance - chapter 6.2.0). The contact of an electrolyte with the solid surface would bring about a preferential migration of ions - usually from the metal into the electrolyte (see double layer chapter 9) - so establishing an interfacial double layer. The material travelling along the underside of the drop on the solid heated surface may shear this interfacial double layer. This however seems highly unlikely as the surface seems more likely to be violently'swept', rather than cut. Only the cutting action is capable of separating the ion layers at the so called "shear plane".

It would seem that charge produced during the Leidenfrost boiling of a saline drop could involve at least five charging mechanisms, two of which (i) & (ii) are solid - solid contact, one of which (iii) crystalline decrepitation, and two involving double layer shearing (iv) & (v) though these latter two are less likely. Table 1 is an attempt to summarise the sequence of drop events with respect to the charging mechanisms operating at each stage. Typical q/m values are included for comparisons

to be made later in the chapter.

Table 1. (The total duration for all 3 stages is 0.6s;from chart record of charging.)

Stage	Mechanism				
	Solid-Solid Contact	Decrepitation	S-S sliding Contact	D L drop surface	D L solution solid interface
Drop contacts surface	$NaCl_s$ to metal (i) q/m typical values $10^{-3}C\ kg^{-1}$				
Skin decrepitates	$NaCl_s$ breaks up	(ii) q/m unknown but from 7 $10^{-4}C\ kg^{-1}$ approx			
'Explosive' particle emission mechanism			NaCls to metal (iii) q/m max. $10^{-3}C\ kg^{-1}$	Drop surface breaks up(iv) typical q/m values $10^{-7}Ckg^{-1}$	Lower drop surface heated surface (v)q/m typical values $10^{-7}C\ kg^{-1}$

It is difficult to disentangle the relative importance of each mechanism but the stage at which each occurs is reasonably certain for the first two after which all three mechanisms may overlap in the behaviour of the drop. It does not appear possible to take this particular stage and resolve it as a sequence and so throw some light on the order of operation of mechanisms (iii),(iv) & (v) - everything as it were happens at once.

Two mechanisms may not in fact exist in the Leidenfrost drop situation viz (iv) & (v), for the reasons given earlier. Thus three solid-solid charging mechanisms appear to be the most likely sources of charge: Solid - solid contact, Solid - solid sliding, Decrepitation (about which little or nothing seems to be known - though exploratory experiments related in chapter 7 showed that high charge values are in evidence.)

10.3.2 Quantitative Speculations.

Lacchia [2] has described experiments in which streams of dry polymer particles (3 to 40 μm radius) and dry glass particles (5 to 50 μm radius) were charged in the course of flow down a metal tube. He attributed the charging to solid - solid contact (triboelectric) and stated that charge per particle is a function of particle radius.

Summary of Lacchia's results :-

Average charge per particle (Glass) 9.25×10^{-16} C

Average charge per particle (Polymer) 4.75×10^{-16} C

$q/m = 2.07 \times 10^{-5}$ C kg^{-1} (Glass)

$q/m = 2.2 \times 10^{-4}$ C kg^{-1} (Polymer)

A net positive polarity was found to exist in the distribution of charges.

Recently (Bright & Cross 1977 [3]) this triboelectric charging mechanism has been used to produce commercial powder coating deposition devices. By optimising the choice of metal and polymer, values of q/m up to 10^{-3} C kg^{-1} have been obtained with a number of polymers including P.T.F.E., epoxy resins and nylon. This appears to be an upper limit; the limiting process being corona discharge from the charged polymer particles.

Double layer charging.

In an investigation of charged water droplets produced by an ultrasonic fountain Bassett (1975)[4] found the average charge per 10μm radius droplet was 4×10^{-19}C. A value which agrees with Blanchard's data for droplets from bursting bubbles[5] in which several experiments yielded charge values ranging from 10^{-19} to 10^{-18}C per 10μm particle. The water droplet cloud in Bassett's investigation had a q/m value of about 10^{-7} C kg^{-1} which is the same order of magnitude to that obtained in the earlier work of Lenard (chapter 9), 10^{-7}C kg^{-1} and more recently Gibson[6] 10^{-7}, 10^{-9} C kg^{-1}. Experiments in which water droplet clouds were produced in connection with investigations of electrostatic hazards with washing of fuel tanks with water jets indicated that similar values of q/m were obtained. In the case of water droplet clouds it was found that a net negative polarity exists in the distribution of charge on individual droplets. Bright[7] has found that the addition of low concentrations of specific chemicals such as surfactants, acids etc., will alter the net polarity.

Summary of values for the Leidenfrost charging process.
Average charge per particle (Na Cl) all radii 10^{-14} C
Average charge per particle (Na Cl) 10μm radius 10^{-17}C
q/m = 2×10^{-3} C kg^{-1}
Charge per particle increased with particle size.
A net positive polarity was found to exist on particle distribution.
Changing surface material from metal to ceramic decreased charge by a factor of 10 (viz 10^{-10} C to 10^{-11} C per particle emission).

There is an obvious difference in charge and q/m values which helps in identifying the mechanism involved. In Table 2 typical values from various processes thought to employ a single mechanism are listed in comparison with Leidenfrost charging - which is thought to employ several mechanisms.

Table 2. A comparative table of results from different mechanisms.

(Particles of average radius 10μ m).

	Solid-solid	Double layer	Leidenfrost
Average charge per particle	10^{-16} C	10^{-19}C	10^{-14}C
q/m	2×10^{-5}C kg^{-1}	10^{-7}C kg^{-1}	2×10^{-3}C kg^{-1}
Net polarity	+	-	+

The triboelectric and solid - solid contact charging of particles yield charges very similar to those of solute particle values obtained from Leidenfrost boiling. On the other hand in a comparison of charge magnitude the charge per particle is higher by a factor of 10^2 to 10^5 than those determined for droplets charged by double layer shearing. The surface material used has been demonstrated to affect the quantity of charge generated in the Leidenfrost charging process. Although Bright has found that specific contaminants will alter the net polarity (see above) and Blanchard also found this to happen when oil was wiped on the hot surface this is a short duration phenomenon and does not prevent the use of net polarity for compararative purposes. In the case of the Leidenfrost process net polarity indicates a solid - solid contact mechanism predominating. This view is supported by a comparison of charge per particle and q/m values both of which also suggest that solid - solid charging mechanisms play a major role in the charging process associated with the Leidenfrost boiling of aqueous solutions.

In a discussion on the Leidenfrost charging process it was suggested by Professor G. Hills (Southampton), that there may be some preferential migration of Cl^- ions across the vapour layer to the metal surface. Na^+ ions remaining in the drop would account for the positive charges on particles. This suggestion, which is a version of the liquid/metal

double layer idea, was later examined by setting up Leidenfrost drops of $Na\ Cl_{aq}$ on stainless steel surfaces and examining these by means of the x - ray probe of a Stereoscan electron microscope. The technique was so sensitive that it revealed that sea water had not been used - there were no Magnesium ions - (the drop solution was 3.5% Na Cl in distilled water). However no evidence was found to support the preferential ion migration hypothesis and only Na and Cl in equal amounts as $Na\ Cl_s$ was found on the surfaces.

In conclusion then the evidence at present available strongly supports the claim that particles from Leidenfrost boiling are charged by solid - solid charging. The (i)(ii)(iii) of section 10.3.1 thus providing the charging mechanisms with the less likely involvement of (iv)(v) double layer shearing mechanisms.

Chapter 10 References.

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11.0.0 The Relevance of the Investigation of a Reproducible Boiling Phenomenon to Volcanic Lightning.

11.1.0 Introduction.

It was stated in the introduction to the first chapter that the investigation evolved out of the laboratory work carried out into saline solution contact charging following studies in the field when lightning was observed above volcanoes. It is now possible, in this chapter, to look back at the earlier studies of saline contact charging (see Chapter 3) and the data from field work on, or in, volcanic clouds and apply the information gained by this investigation of a reproducible boiling phenomenon. The outcome of such application will emphasise the importance of the Leidenfrost form of boiling of aqueous solution even to the extent of suggesting that in situations where solution to lava contact is in evidence this is the major contributory charging process and that the 'Blanchard Effect' is itself of this form.

11.1.1 The Leidenfrost charging process considered with respect to earlier investigations of saline contact charging and also to the clouds associated with volcanic lightning.

The laboratory investigation of saline solution contact charging made by Blanchard and dealt with in chapter 3 gave the following results:- A drop 4.2 mm diameter gave a cloud of volume about 2×10^3 cm^3 with a charge of +15 esu (5×10^{-9}C, 2.5×10^{-6}C m^{-3}). From this information Blanchard and others (see chapter3) estimated an average charge per particle of 5×10^{-19}C. The present author has previously made some criticism of the method used by Blanchard et al to obtain this value (3.3.1). They assumed that the boiling phenomenon observed in Blanchard's investigation was identical to that used by Woodcock & Spencer and thereby produced particles in the same numbers as they reported for flash boiling. But simple observation shows that

a large drop fragments - in the Blanchard effect - into tiny bouncing droplets and does not spread out and wet the surface as in flash boiling. The droplets retain their drop like configuration and boil by Leidenfrost boiling (It was indeed this observation which launched the author's own investigation presented here).

If we consider, following Bright, the normal droplet density of a cloud to be 10^5 droplets cm^{-3} and each droplet in the cloud to be 10 μm radius (the smaller droplets having evaporated and those of larger radius having settled out) then a cloud having a volume of 2×10^3 cm^3 will have a droplet population = $2 \times 10^3 \times 10^5 = 2 \times 10^8$ droplets. Since the total charge on the cloud is 5×10^{-9}C then the average charge per particle on 10 μm radius particles is $\frac{5 \times 10^{-9}\text{C}}{2 \times 10^8}$ per particle, which is 2.5×10^{-17}C.

This value is of the same order of magnitude to that found on particles from Leidenfrost boiling and it leads me to suggest that the Leidenfrost phenomenon is more likely than flash boiling, and that the formerly discounted Leidenfrost phenomenon as a generator of charge plays an important role in the production of highly charged particles.

The surface temperatures, estimated to be 200°C to about 300°C, stated by Blanchard to be those in which he observed a saline drop to bounce and fragment correspond to the part nucleate, Leidenfrost boiling - or transition boiling - considered in 4.2.4. It does seem very likely that the 'Blanchard effect' occurs because the larger drop, due to Taylor instability, touches the hot surface and fragments. Although the surface is not high enough to establish Leidenfrost (film - boiling 4.2.4) with the large drop it is able to do so with some of the many tiny drops which have been observed to glide on the hot surface. The temperatures stated by Blanchard are in the so called 'transition boiling regime' since there is no one Leidenfrost point i.e. temperature for water. If either the 'Blanchard effect' - a form of Leidenfrost

boiling - or Leidenfrost boiling in its more common form are operating independently or in conjunction (their relative importance determined by the surface roughness and temperature of the lava) then particles having high values of charge, e.g. 10^{-17} to 10^{-15} C as against 10^{-19} C, will be in evidence in the cloud.

Fig. 1 Summary of charge densities reported from volcanic clouds.

2.3×10^{-9} C m^{-3} Mt. Azuma (Ishikawa et al, chapter 1 ref. 20)

10^{-8} to 10^{-7} C m^{-3} Surtsey crater orifice (Anderson et al chapter 3 ref3)

10^{-7}C m^{-3} Surtsey - steam cloud at sea/lava interface (Anderson).

(Compare these values with normal atmospheric space charge density which is 10^{-11} C m^{-3} Mason(1))

The high average charge values found on Leidenfrost particles (10^{-14}C) mean that a number density 2×10^{-5} smaller than that needed for particle values (calculated by Blanchard (10^{-19}C) would be sufficient to produce the cloud charge densities found in volcanic clouds (Fig.1). Whereas previously it had been stated that a large number of particles each carrying a small charge, produced by an assumed flash boiling process, were needed, it is here demonstrated that a small number of particles each carrying a high charge, produced by the Leidenfrost boiling process, will produce the charge densities in clouds associated with volcanic lightning.

11.2.0 Conclusion.

The phenomenon of boiling first published by J.G. Leidenfrost as a part of his, possibly alchemical, researches into the behaviour of water in a hot spoon has been discovered to have an important charging process associated with it as well as being a source of solute particles when an aqueous solution replaces the water. These electrically charged particles are involved in the magnificent natural display of volcanic lightning when aqueous solution in contact with heated lava is involved.

It would be possible to speculate on possible future implications of the production of charged particles of solute emitted from Leidenfrost drops in such fields as hazards/pollution, bio-synthesis, matter / antimatter cosmology and electrostatics generally but this would be to generalise too much at this juncture and must remain for some future date.

Chapter 11 References.

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Acknowledgements.

'No man is an island intire of itself'.

John Donne

The work for this thesis was pursued part-time and to a considerable extent in isolation. It is only when one comes to acknowledge the help of others that the full realisation strikes home of the number of people involved and of the inadequacy of words to thank them. I am indebted to the Open University for allowing me the opportunity to be a research student. My tutors Dr.W.A. Cooper and Professor A.W. Bright have shared the exhilaration of success and been a support in times of depressive failure in addition to supplying resources, apparatus and facilities. Their advice and guidance tempered my sometimes naïve ideas through the work and they supplied tuition without pedanticism which enabled my enthusiasm and interest to be directed into the investigation without undue restriction. In so doing they have opened my eyes to the world of science for which I can never thank them enough. Dr. D.C. Blanchard has maintained a lengthy correspondence and made a personal visit which gave a great boost to my morale particularly as he said he would not continue his own research on the subject of saline contact charging thereby relieving my mind of some anxiety. My thanks are due also to many people who have exchanged letters, in particular, Professor K.J. Bell, Professor C.B. Moore, Professor A.D. Moore (who has also made two personal visits), Professor S. Thorarinsson, To members of Southampton University,Dept. of Electrostatics,Dr.J. Bassett & Mr.I. Parker for help and encouragement during my visits there. Thankyou to the scientific scholars long dead the search for whose papers inspired my interest in the history of science, and to ——————— the staff and children of Kensington Junior School, Ilkeston. And last most deserving of my thanks and gratitude my wife Judith Ann and my daughters Julia Ann and Rosalind Elizabeth who have tolerated an apparent eccentric in their midst and permitted a part of the house to be given over to the equipment necessary to investigate the charged particles from boiling solutions on heated surfaces.

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